



TECHNICAL MEMORANDUM

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Company: Monsanto

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RE: EVALUATION OF NATURAL ATTENUATION CONTROLS – MONSANTO SODA SPRINGS SITE

1.0 INTRODUCTION

The Record of Decision (ROD) for the Monsanto site selected monitored natural attenuation with institutional controls as the groundwater remedy (EPA, 1997). In a communication with Monsanto, EPA has commented that natural attenuation may not be effective at preventing the migration of some constituents of concern (COCs), at concentrations exceeding remedial goals, offsite. The objective of this memorandum is to evaluate the Monsanto groundwater quality data to determine the potential for natural attenuation of the five COCs: cadmium (Cd), manganese (Mn), fluoride (F), selenium (Se) and nitrate (NO_3).

2.0 BACKGROUND

The ROD established groundwater remediation goals for five COCs at the Monsanto site: cadmium, fluoride, nitrate, selenium and manganese (EPA, 1997). These remediation goals are the Maximum Contaminant Levels (MCLs) under the Safe Drinking Water Act for all constituents with the exception of manganese (Table 1). The manganese limit is a risk-based concentration.

TABLE 1
Remediation Goals for Constituents of Concern (COCs)

Constituent of Concern (COC)	Remediation Goal (mg/L)
Cadmium (Cd)	0.005
Fluoride (F)	4
Nitrate (as N) or Nitrate as (NO_3)	10/44
Selenium (Se)	0.05
Manganese (Mn)	0.18

The following three major source zones have been identified on site: the former Underflow Solids Ponds, the Northwest Pond, and the Old Hydroclarifier. The Northwest Pond (now a permitted solid waste landfill) and the Old Hydroclarifier were located to the east of the Monsanto Fault. The Underflow Solids

Ponds were located on the west side of the Plant and were closed in 1987/1988 by filling with molten slag and placement of a bentonite cap.

The primary hydrostratigraphic zones underlying the Monsanto Plant include the Upper Basalt Zone (UBZ) and the Lower Basalt Zone (LBZ). The principal aquifer is the UBZ, which extends to a depth of about 100 feet below ground surface (bgs) below the plant, and it is the aquifer affected by Monsanto activities. The depth to the water table ranges from 20 feet bgs in the northeast corner to 100 feet bgs in the center of the plant. Groundwater flow in the UBZ is a function of faulting, regional hydrogeologic conditions, and pumping of the plant production wells. The UBZ is broken into smaller regions (UBZ-1 through UBZ-4), based on hydrogeological controls and groundwater quality. UBZ-2 and UBZ-4 have been identified as the most impacted groundwater zones within the UBZ since the three major source areas have been identified within these zones: the former Underflow Solids Ponds (UBZ-2), and the Northwest Pond and the Old Hydroclarifier (UBZ-4; Golder, 2003). This memorandum therefore focuses on groundwater quality conditions in the UBZ-2 and UBZ-4.

The UBZ monitoring wells that are located in proximity to and down-gradient of each source area are listed in Table 2 and shown in Figure 1.

TABLE 2
Source Area Monitoring Wells

Source	Upper Basalt Zone Wells (UBZ)	Distance Down-gradient from Source Area (ft)
Northwest Pond	TW-16 TW-17	125 125
Old Hydroclarifier	TW-40	60
Former Underflow Solids Ponds	TW-22 TW-24 TW-37	1,115 1,115 <50

This memorandum evaluates the temporal and spatial trends in groundwater quality for the UBZ source zone area wells and downgradient wells to assess the mobility of the COCs and the potential for natural attenuation.

3.0 EPA NATURAL ATTENUATION GUIDANCE

The Environmental Protection Agency (EPA) provides guidance for monitoring the natural attenuation of inorganic contaminants in groundwater. The document titled "*Monitored Natural Attenuation of Inorganic Contaminants in Ground Water*" (EPA, 2007), provides information on the different chemical and physical mechanisms responsible for natural attenuation for a number of COCs. It is a technical document that

provides guidance in the determination of whether natural attenuation can be considered to be effective as a remedial approach for inorganic contaminants in groundwater.

The EPA defines natural attenuation processes as those that “*reduce mass, toxicity, mobility, volume or concentration of contaminants*”. The document focuses on selected contaminants (i.e., arsenic, cadmium, chromium, copper, lead, nickel, nitrate, perchlorate, and selenium) based on: their presence at Superfund sites; their identification as primary COCs based on toxicity, industrial use, and frequency of occurrence at Superfund sites; and, their geochemical behavior, considering toxicity, ion charge, transport behavior, and redox chemistry. The EPA document therefore addresses three of the five COCs at the Monsanto Site (cadmium, nitrate and selenium).

The attenuation of contaminants in groundwater may occur due to a number of chemical, biological, and physical processes, including dispersion, sorption, ion exchange, secondary mineral precipitation, biodegradation, and redox reactions. Dispersion in a homogeneous isotropic aquifer will affect all parameters equally. The degree to which the other processes in combination affect the mobility of a particular constituent defines the constituent’s transport velocity.

For inorganic constituents, the primary attenuation mechanisms are often sorption onto aquifer solids and secondary mineral precipitation. Both these mechanisms result in partitioning of the constituent from the aqueous to the solid phase. For inorganic constituents, the EPA therefore considers the existence of two distinct plumes within the boundary of the groundwater plume as follows (EPA, 2007, Figure 2): (1) a dissolved mobile (i.e., faster) plume; and, (2) a solid phase or immobile (i.e., slower) plume resulting from partitioning of the contaminant to the solid phase. The dissolved or mobile plume includes contaminants associated with mobile colloids.

For inorganic contaminants, the EPA defines the following two objectives for effective natural attenuation (EPA, 2007):

- Demonstration of removal of the inorganic contaminant from the dissolved phase leading to a stable or shrinking groundwater plume; and,
- Demonstration of stabilization of the inorganic contaminant immobilized onto aquifer solids such that the future re-mobilization will not occur to a level that threatens the health of environmental receptors.

3.1 EPA Recommended Approach to Site Characterization

EPA recommends the following four-tiered analysis approach for the collection and evaluation of data to assess the effectiveness of natural attenuation (EPA, 2007).

1. Demonstration that the groundwater plume is not expanding and that sorption¹ of the contaminant onto aquifer solids is occurring where immobilization is the predominant attenuation process;
2. Determination of the mechanism and rate of the attenuation process;
3. Determination of the capacity of the aquifer to attenuate the mass of contaminant within the plume and the stability of the immobilized contaminant to resist re-mobilization; and,
4. Design of a performance monitoring program based on the mechanistic understanding developed for the attenuation process, and establishment of a contingency plan tailored to site-specific characteristics.

For each step, the EPA defines the objectives and the types of site-specific data required for the analysis. This memorandum includes Tier I and II analyses.

3.2 Constituent Fate and Transport

The fate and transport of a constituent in groundwater is a function of the physical, chemical, and biological characteristics of the aquifer. The importance of each of these factors on constituent mobility is summarized in Table 3.

TABLE 3
Constituent Fate and Transport

Physical Transport Mechanism	Groundwater flow and solute movement	<p>Advection: Advection is the movement of a solute with the bulk movement of groundwater and is the primary solute transportation mechanism.</p> <p>Dispersion: During advection, the solute will spread to occupy a larger portion of the flow field in the direction of the groundwater flow and perpendicular to it. This results in mixing of the groundwater reducing the solute concentration.</p>
	Colloidal transport of inorganic constituents	<p>Presence of colloids, particles of a diameter less than 10 microns, is a possible transport mechanism in groundwater. Under the appropriate conditions may be significant for the transport of some constituents, affecting migration and transport model predictions. Although colloid migration is likely to occur, it is not considered to be a dominant mechanism for constituent migration.</p>
Sorption to aquifer solids	Adsorption	<p>Adsorption occurs when a dissolved constituent becomes attached to the surface of a solid present in the aquifer. The strength of the binding will depend upon the characteristics of the adsorbate, the sorbent, and the groundwater chemistry.</p>
	Precipitation	<p>Precipitation is a result of the oversaturation of a mineral phase in solution. It is a very important immobilization mechanism for inorganic compounds in groundwater. Precipitation can involve four different processes: precipitation from solution, co-</p>

¹ Sorption is used to collectively represent all mechanisms that result in partitioning of the constituent from the aqueous to the solid phase.

		precipitation, surface precipitation, and mineral transformation (evolution of a metastable precipitate towards a more stable mineral phase). All processes present different characteristics, but they all produce a reduction in the levels of constituents in solution.
Microbial Impact	Microbial control on redox state	The metabolic reaction of microorganisms may exert significant influence in the redox conditions of the aquifer, which at the same time can control the precipitation-dissolution reactions, which, in turn, can influence the adsorption properties of some constituents.
	Constituent speciation and attenuation	Through metabolic reactions, microbes are able to transform metals and metalloids, thereby affecting constituent mobilization/immobilization, precipitation, adsorption, and intracellular accumulation. The main mechanisms by which microbes may transform metals include: oxidation and reduction reactions, biosorption, and methylation and demethylation processes.

The factors most likely to affect the mobility of COCs at the Monsanto site, based on the information provided by the EPA (2007) and previous reports (Golder, 2002), are summarized in Table 4.

TABLE 4
COC Natural Attenuation Controls

NATURAL ATTENUATION MECHANISMS					
Constituent	Dispersion	Colloidal transport	Adsorption	Precipitation	Microbial impact (redox conditions)
Cadmium (Cd)	X	X	X	X	
Manganese (Mn)	X			X	X
Fluoride (F)	X		X	X	
Selenium (Se)	X		X	X	X
Nitrate (NO₃)	X				X

A brief summary of the mobility of each of the COCs follows. Controls on mobility occurring at the Monsanto site are discussed in Section 5.

- **Cadmium** – Cadmium exists in the +2 valence state. It is adsorbed by oxides of aluminum, iron, and manganese and also by calcite. The adsorption edge for cadmium occurs at a higher pH than that of lead, copper, and zinc (EPRI, 1984). In groundwater, otavite (CdCO₃) precipitation may control cadmium concentrations. Review of three widely accepted geochemical databases (WATEQ, PHREEQC, and MINTEQA4) indicates a range of solubility constants for otavite from 10^{-13.74} to 10⁻¹². Mineral and organic particles can participate in colloidal transport of cadmium and can be significant in groundwater systems. Cadmium adsorbed to colloidal hydrous ferric oxides may subsequently desorb due to changes in pH or oxidation-reduction potential (EPA, 2007).
- **Manganese** – Manganese may exist in five valence states: +2, +3, +4, +6, and +7. Manganese mobility is redox dependent, exhibiting greater mobility under reduced

conditions. Under oxidizing conditions, aqueous manganese concentrations may be reduced by the precipitation of oxides and hydroxides. Manganese concentrations may also be controlled by the precipitation of rhodochrosite (MnCO_3 , EPRI, 1984).

- **Fluoride** – Fluoride exists in the -1 valence state. In calcareous soils and sediments, fluoride concentrations may be controlled by the mineral fluorite (CaF_2). Fluoride is not strongly adsorbed by soils; however, adsorption is greatest at pH values between approximately 4 and 6.5. Fluoride forms strong complexes with aluminum (EPRI, 1984).
- **Selenium** – In nature, selenium can exist in four valence states: -2 , 0 , $+4$ and $+6$. In oxidized waters at neutral pH, selenium will exist as an anion. Selenium ($+6$) will be predominantly present as SeO_4^{2-} and selenium ($+4$) will be present as HSeO_3^- . Above approximately pH 7.6, selenium ($+4$) is predominantly present as SeO_3^{2-} . Selenate, selenium ($+6$), species are considered quite mobile, especially in alkaline conditions. Selenite, selenium $+4$, species are significantly less mobile. Reducing environments favor the formation of elemental selenium, selenium (0), and selenide, selenium (-2). Elemental selenium is insoluble. Selenide, which forms sparingly-soluble minerals such as FeSe_2 and FeSe , is immobile in most aquifers.

Selenium will adsorb to both aluminum and iron hydrous oxides and amorphous aluminosilicates. Because selenium exists as an anion in solution, maximum selenium adsorption occurs at low pH, reducing its mobility. Selenium ($+4$) is reported to adsorb more strongly to hydrous iron oxides than selenium ($+6$). The opposite behaviour has been observed for clay minerals, that is, $\text{Se}(+6)$ is more strongly adsorbed than $\text{Se}(+4)$. Sulfate has been reported to compete with selenium for adsorption sites (EPRI, 1984).

- **Nitrate** – Nitrate is mobile in groundwater and is transported in groundwater systems with little or no retardation (Freeze and Cherry, 1979).

4.0 SITE GROUNDWATER QUALITY

Groundwater flow in the UBZ is influenced by faulting, regional hydrogeological conditions, and pumping of plant production wells. The groundwater flow direction beneath the site is generally from north to south paralleling the geological structures.

4.1 UBZ-2 Trends

Groundwater velocity in the UBZ-2 is estimated at approximately 1.3 feet/day (Golder, 2008). Therefore, the groundwater travel time from the source area (former Underflow Solids Ponds) TW-37 to TW-54 (located south of the Plant Fence Line) is estimated at approximately 10 years.

Table 5 presents a summary of the general groundwater quality trends over the last 10 years in the UBZ-2 wells for the five COC's, and chloride and sulfate. Chloride and sulfate are included because they are indicators of mobile groundwater constituent transport. Wells are listed in order of the direction of groundwater flow (i.e., from upgradient to downgradient). General trends were determined by a visual assessment of chemical hydrographs and are classified as increasing (\uparrow), decreasing (\downarrow) or stable ($=$). For several wells, two trends are shown. These represent the general trend over the first and the second five-year period. The three wells located in proximity to the former Underflow Solids Ponds are shaded gray. Table 5 also presents the most recent groundwater quality results from May/June 2009. COC concentrations that exceed the remediation goal are shown in bold type.

TABLE 5
Current UBZ-2 Constituent Concentrations and Groundwater Quality Trends Over the Last 10 Years

Well	Distance from Source (ft)	Cl (mg/L)	SO ₄ (mg/L)	NO ₃ as N (mg/L)	Cd (mg/L)	Mn (mg/L)	F (mg/L)	Se (mg/L)
Remedial Goal (mg/L)				10	0.005	0.18	4	0.05
TW-57	850 (Up)	= 15	↓ 69	= 1.3	= ND	= ND	= 0.43	= 0.004
TW-37	Source (<50)	↑ 508	↑= 317	↑= 9.4	↑ 0.96	= 0.71	↓ 9.3	=↓ 0.23
TW-22	1,115	↓= 26	↓= 130	↓= 4.3	= 0.023	= 0.79	↓= 3.0	↓ 0.13
TW-24	1,115	= 80	↓= 179	↓= 5.0	= 0.29	= 0.28	↓= 4.6	↓ 0.23
TW-39	3,600	↓↑ 135	↓↑ 647	↓↑ 8.6	= 0.017	= ND	↓↑ 3.3	↓↑ 0.43
TW-35	3,600	= 36	= 127	= ND	= 0.0003	= 0.15	= 0.15	= 0.0008
TW-20	3,750	↑↓ 84	↑↓ 467	↑↓ 8.8	↑↓ 0.003	= ND	= 2.1	↑↓ 0.1
TW-34	3,750	= 35	= 148	= 0.09	= ND	= 0.18	= 0.38	= 0.005
TW-54	4,600	↑= 82	↑= 377	↑↓ 6.8	= ND	= 0.003	↓↑ 2.8	↑=↓ 0.14
TW-55	4,700	= 45	↑= 161	= 3.1	= ND	= ND	=↑ 0.71	↑↓ 0.03
TW-62	5,700	= 76	= 344	= 4.9	= ND	= ND	= 0.23	↑ 0.13
TW-59	6,900	= 64	= 279	= 5.0	= ND	= ND	= 0.23	↑ 0.1
Lewis	6,750	= 45	= 151	= 9.0	= ND	= ND	= 0.62	= 0.014

ND – non-detect.

Values shown in bold type exceed the remediation goal. No remedial goal for chloride and sulfate.

Chemical hydrographs for selected wells from Table 5 are shown in Figures 3 through 8. For each constituent, an “a” and “b” figure is presented. The “a” series figures present the water quality data as measured. For the “b” series figures, the temporal scale for some wells has been modified based on the estimated groundwater velocity to allow for direct comparison of the concentration trends among wells. For example, Figure 3a presents chloride, sulfate, and nitrate concentrations for the three source area wells (TW-37, TW-22 and TW-24). Figure 3b presents the same data; however, results for well TW-37 have been projected forward in time to show the concentrations assuming the plume migrated from TW-37 to TW-22/TW-24 over a period of 2.8 years (consistent with the estimated groundwater velocity).

Concentrations of all constituents have remained stable in the upgradient (background) well (TW-57). Two of the source area wells (TW-22 and TW-24) currently demonstrate stable or decreasing concentration trends for the seven constituents listed in Table 5. Wells TW-22 and TW-24 generally

report similar groundwater quality trends and concentrations. Figure 3a illustrates the similarity in TW-22 and TW-24 chloride, sulfate, and nitrate concentrations. The third source area well, TW-37, currently demonstrates stable or decreasing concentration trends for sulfate, nitrate, selenium, fluoride, and manganese; however, chloride and cadmium concentrations are currently increasing.

The chloride concentration measured at TW-37 in May 2009 (508 mg/L) was higher than concentrations measured historically. In addition to chloride, magnesium concentrations are also increasing in TW-37. A Piper plot of TW-37 groundwater major ion chemistry over time shows a distinct change in the major ion chemistry at this well beginning in approximately 2006 (Figure 9a; alkalinity and other major cations were not measured from 2002 to 2006). TW-37 water quality has evolved from a Ca-Mg-HCO₃-SO₄ type water to a Ca-Mg-Cl-SO₄-HCO₃ type water. The major ion signature of TW-37 is distinct from the other UBZ-2 wells (Figure 9b). The observed increase in chloride at TW-37, in the absence of concentration increases for other constituents typically associated with the former Underflow Solids Ponds source, may be indicative of a new source of chloride loading to the UBZ-2.

Magnesium chloride is used for dust control on the roads at the Plant. Applications have increased from two applications per year prior to 2006 to three times a year. Magnesium chloride is highly soluble and is transported through the vadose zone by infiltrating water (Heffner, 1997). The movement is largely dependent upon the rate and frequency of rainfall, the drainage characteristics of the area, and the chemical and physical nature of the soil. During periods of light rainfall (i.e., low infiltration), the magnesium chloride remains as a hydrated complex and moves vertically within the soil surface moisture. During wet periods, magnesium chloride will penetrate to greater depths. Lateral movement occurs, but at a much lower rate. With rainfall, and depending on the permeability of the soil, magnesium chloride can migrate considerable distances either as runoff or as an infiltrating fluid reaching groundwater.

Based on the water quality observed at TW-37, it appears that the application dust suppressant may have impacted the quality of the groundwater in some areas of the Monsanto site. As shown on Figure 9a, the major anion signature at TW-37 has changed during the past five years. During the late 1990s and early 2000s, chloride concentrations at TW-37 were stable at approximately 30 mg/L. Since the mid 2000s, chloride concentrations have increased to 500 mg/L. During this same time period, magnesium concentrations have increased from approximately 60 mg/L to 125 mg/L. The observed coincident increase in chloride and magnesium concentrations may be the result of infiltration of dust suppressant compounds into the groundwater system.

In addition to chloride and magnesium, calcium and cadmium concentrations have also increased in recent years at TW-37. The observed increases in chloride, magnesium and calcium could indicate loading from a dust suppressant source. If a dust suppressant is the source of the observed chloride trends, the observed increases in cadmium concentrations could be attributed to dissolution of previously precipitated otavite (cadmium carbonate). During the late 1990s and early 2000s, TW-37 cadmium

concentrations were stable at approximately 0.35 mg/L. The recent increase in chloride concentrations at TW-37 would result in an increase in the solubility of otavite promoting dissolution of this mineral phase (see Figure 13).

In addition to TW-37, several other wells have shown increases in chloride concentrations (albeit not as large as those observed at TW-37) beginning in 2005. Increasing magnesium concentrations have also been observed in some of these wells. Table 6 presents the wells that exhibit changes in chloride and magnesium trends during the last ten years.

TABLE 6
Wells with Changes in Chloride and Magnesium Trends

UBZ-2			UBZ-4		
Well	Cl	Mg	Well	Cl	Mg
Lewis	=	↑(99-05) ↓(06-09)	PW-01	↑(05 -09)	↑(06 -09)
TW-20	↑(99-05) ↓(06-09)	↑(99-05) ↓(06-09)	PW-02	↑(05 -09)	=
TW-24	↓(05-08) ↑(08-09)	↓(05-07) ↑(07-09)	PW-03	↑(05 -09)	↑(04 -09)
TW-34	=	↑(99-09)	PW-04	=	=
TW-37	↑(05 -09)	↑(05-09)	TW-16	↑(05 -09)	=
TW-39	↑(05 -09)	=	TW-17	↓(01-09)	↑(99 -09)
TW-54	=	↓(05-09)	TW-29	↑(05 -09)	=
TW-55	=	↑(02 -07)	TW-40	↑(03 -09)	=
TW-57	=	↓(04-09)	TW-50	↑(02 -09)	↑(07 -09)

The groundwater quality at wells which exhibit a coincident increase in magnesium and chloride concentrations may be affected by dust suppressant. In the UBZ-4, increased chloride and magnesium concentrations in PW-01, PW-03 and TW-50 suggest possible impacts from dust control agents starting in most cases about five years ago. In addition to chloride and magnesium, sulfate concentrations also currently demonstrate an increasing trend at TW-50 and PW-01 and PW-03; whether this increase is attributable to dust suppression or other factors is not known at this time.

Table 5 shows which UBZ-2 wells currently exceed the remedial goals for the five COCs. Wells TW-35 and TW-34 are screened in deeper basalt interflows between the UBZ and LBZ. Groundwater quality in these wells has been stable over the period of record indicating no significant impact to groundwater quality from the former Underflow Solids Ponds. These wells are therefore excluded from the following discussion of COC concentration trends.

- **Nitrate** – Nitrate concentrations are below the remedial goal in all wells listed in Table 5. The nitrate plume extends to the southern-most wells (TW-59 and Lewis).
- **Cadmium** – Cadmium concentrations in the source area wells currently range from approximately 0.02 (TW-22) to 1 mg/L (TW-37). Groundwater cadmium concentrations decrease with distance from the source area wells. Cadmium is below detectable limits in the southern-most wells (TW54, TW55, TW-62, TW-59, and Lewis).

- **Manganese** - Manganese concentrations have been relatively stable for the last 10 years in all the UBZ-2 monitoring wells. Concentrations in the source area wells currently range from approximately 0.3 (TW-24) to 0.8 mg/L (TW-22). Groundwater manganese concentrations are below the remedial goal in the downgradient wells.
- **Fluoride** – Fluoride concentrations in the source area wells currently demonstrate a stable or decreasing trend. Fluoride concentrations are currently stable in most of the downgradient wells and are below the remedial goal.
- **Selenium** – Selenium concentrations in the source area wells currently range from 0.1 (TW-22) to 0.2 mg/L (TW-24 and TW-37) and demonstrate a stable or decreasing trend. Similar to nitrate, the selenium plume extends to the southern-most wells.

4.2 UBZ-4 trends

Table 7 presents the trends for the last 10 years in selected wells in the UBZ-4 area for the COCs, and for chloride and sulfate. Wells are listed in order of the direction of groundwater flow (i.e., from upgradient to downgradient). General trends were determined by a visual assessment of chemical hydrographs and are classified as increasing (↑), decreasing (↓) or stable (=). For several wells, two trends are shown. The three wells located closest downgradient of the sources are shaded gray. Table 7 also presents the most recent groundwater quality results from May/June 2009. COC concentrations that exceed the remediation goal are shown in bold type.

TABLE 7
Current UBZ-4 Constituent Concentrations and Groundwater Quality Trends Over the Last 10 Years

Well	Source Area	Distance from Source (ft)	Cl (mg/L)		SO ₄ (mg/L)		NO ₃ as N (mg/L)		Cd (mg/L)		Mn (mg/L)		F (mg/L)		Se (mg/L)	
	Remedial Goal (mg/L)						10		0.005		0.18		4		0.05	
TW-29	Background	60 (Up)	↑	85	=	93	=	4.4	=	ND	=	ND	=	0.20	=	0.009
SO2 N	Background	1,800 (Up)	=	23	=	44	↑↓	15.3	=	ND	=	ND	=	0.46	=	0.003
TW-48		1,250 (Up)	=	14	=	68	↑	4.8	↑↓	ND	=	ND	=	0.24	=	0.002
PW-04	Background	1,100 (Up)	=	13	=	67	=	4.2	=	ND	=	ND	=	0.26	=	0.002
TW-49		1,050 (Up)	=	23	=	81	=	3.6	=	ND	=	ND	=	0.25	=	0.002
TW-16	NW Pond	125	=↑	92	=↑	197	=↑	5.0	=	0.4330	=	ND	↓	2.00	=↓	0.132
TW-17	NW Pond	125	↓	2	↓	163	=	0.1	=	0.0028	↑	2.810	=	1.50	=	0.007
TW-50		1,400	↑	213	=↑	452	=	1.0	↑↓	0.0055	↑	0.610	=	0.46	↑	0.046
TW-40	Old Hydroclarifier	60	=↑	446	↓↑	860	↑	19.3	=	2.02	=	0.027	↓	2.92	=↓	0.571
TW-43		30	=	310	=	654	↑↓	11.9	=	1.67	=	0.005	=	5.68	=↓	0.578
TW-26		1000	↓	297	↓↑	435	↑	4.96	=	ND	↓	0.55	↑	1.98	↑	0.298
PW-01		800	↑	185	↓↑	229	↑	4.9	↓↑	0.0589	=	ND	=	0.83	=	0.069
PW-02		1,350	↑	78	=↑	171	↑	4.6	=↑	0.0060	=	ND	=	0.44	=	0.023
PW-03		1,600	=↑	92	=↑	161	↑	4.3	=	0.0016	=	ND	=	0.49	=	0.017

ND – non-detect.

Values shown in bold type exceed the remediation goal. No remedial goal for chloride and sulfate.

During the last 10 years, 7 of the 14 wells located in the UBZ-4 have shown an increasing trend in the chloride concentration, however only two of them have shown similar trend in cadmium, and one has a presently decreasing trend (TW-50). The increasing trends for PW-01, 02, and 03 could be explained by the arrival of a chloride plume, while wells TW-16, 40, and 50 are located near the source areas. The increasing trend for well TW-29 would not be explained by arrival of a plume since it is located upgradient from the source areas.

Sulfate has demonstrated increasing concentration trends at the same wells as chloride with the exception of TW-29, well located in the northwest corner of the plant, with the increases beginning around 2007 for all wells. Of the 14 wells presented in Table 7, only two wells (TW-17 and TW-50) show increases in manganese, the rest have demonstrated stable concentration trends over the last ten years. Fluoride has demonstrated stable concentration trends during the last 10 years with wells TW-16 and TW-40 showing decreases, and well TW-26 showing increases.

The following is a summary of the COC concentration trends over the last ten years:

- **Nitrate** – Nitrate concentrations are below the remedial goal in almost all wells listed in Table 7. Exceptions are well SO2-N (a background well), TW-40, and TW-43. The nitrate plume extends to the west of the source not affecting other wells.
- **Cadmium** – Measured cadmium concentrations in the two source area wells currently range from 0.0028 (TW-17) to 2.02 mg/L (TW-40). Groundwater cadmium concentrations decrease with distance from the source area wells.
- **Manganese** – Manganese concentrations have been relatively stable for the last 10 years in all the UBZ-4 monitoring wells, with the exception of source area well TW-17 and the downgradient well TW-50. The current concentration in the source area well TW-17 is approximately 2.8 mg/L. With the exception of TW-50 and TW-26, manganese concentrations are below the remedial goal in the downgradient wells.
- **Fluoride** – Fluoride concentrations in the source area wells currently demonstrate a stable or decreasing trend. Fluoride concentrations are currently stable in most of the downgradient wells and are below the remedial goal, with the exception of well TW-43, where the concentration is approximately 5.7 mg/L.
- **Selenium** – Selenium concentrations in the source area wells zones currently range from 0.007 (TW-17) to 0.57 mg/L (TW-40) and demonstrate a stable or decreasing trend.

5.0 NATURAL ATTENUATION ASSESSMENT

5.1 Plume Stabilization

The establishment of a stable or steady-state constituent plume is a primary indication that natural attenuation is occurring within a groundwater system. To establish steady-state conditions, source concentrations (and loading) must be stable or declining.

Within the UBZ-2, two of the source area wells demonstrate stable or decreasing concentration trends (i.e., TW-22 and TW-24). The third source area well (TW-37) currently demonstrates increasing concentration trends for the COCs cadmium and nitrate, and also for chloride and sulfate.

In the UBZ-4, down-gradient of the Northwest Pond, (wells TW-16 and 17), cadmium, fluoride and selenium show stable or decreasing trends. In TW-16, chloride, sulfate and nitrate show an increasing trend, while manganese is stable. TW-17 shows an increasing trend only for manganese, while chloride, sulfate and nitrate have shown stable or decreasing trends.

Source area well TW-40 has shown increasing trends for chloride, sulfate and nitrate, while cadmium, manganese, fluoride and selenium have stable or decreasing trends.

Isopleth maps for the five COCs created from 2002 and 2007 groundwater quality data were presented in the second five year review report (Figures 7 to 14; Golder, 2008). These figures were used to assess the stability of constituent plumes between 2002 and 2007. A visual assessment of the relative stability of each contaminant plume was made and is presented on Table 8.

TABLE 8
Plume Stability for COCs

Constituent	Figures	Comment on Plume Stability	
		UBZ-2	UBZ-4
Nitrate	10a and 10b	advancing – unstable	advancing – unstable (hydraulic control)
Selenium	11a and 11b	advancing – unstable	hydraulic control
Cadmium	7a and 7b	stable	stable
Fluoride	8a and 8b	stable	stable
Manganese	9a and 9b	stable	stable

On the basis of plume stabilization, natural attenuation is likely not occurring for nitrate and selenium. The elevated concentrations of nitrate in background wells indicates a nitrate source from agricultural activities up-gradient of the Plant affects groundwater on and to the south of the Plant site. This includes groundwater quality in both the UBZ-2 and UBZ-4 zones. The former sewage lagoon was a source of nitrate but was closed by capping with molten slag over ten years ago. It is believed that off-site agricultural activities are a significant contributor to on-site elevated nitrate concentrations.

5.2 Dispersion

Dispersion and diffusion are two processes that can result in a reduction in constituent concentrations. Diffusion is generally a slow process, and in areas of high groundwater flow velocities such as the Monsanto site, the effect of diffusion on solute concentrations is generally masked by the effect of groundwater movement. Dissolved constituents are transported with the groundwater flow (advective transport). Differences in groundwater velocity along a flow path as well as variable flow path lengths

result in dispersion. Dispersion (or mixing) results in a decrease in solute concentration and occurs in both the direction of groundwater flow (longitudinal dispersion) and in directions normal to the groundwater flow path (transverse horizontal and transverse vertical dispersion).

Chemical hydrographs for constituents that are transported conservatively (i.e., at the average groundwater velocity) were evaluated to assess the effect of dispersion on all constituent concentrations. Time adjusted chloride concentration trends for the UBZ-2 aquifer (Figures 3b and 6b) indicate little to no reduction in chloride concentrations along the groundwater flow path. Similar behavior is observed for sulfate and nitrate. Dispersion is therefore not significant within the UBZ-2 aquifer.

In the UBZ-4 aquifer, there is a considerable reduction in sulfate, chloride, and nitrate between the source area well TW-40 and downgradient pumping wells PW-01 and PW-02 (Figure 10). Dispersion is occurring given the lower concentrations observed in the downgradient wells. Much of this dispersion is likely attributed to greater mixing due to pumping.

5.3 Sorption

The process by which a solute becomes distributed between the groundwater and the aquifer materials is called partitioning, described by a partition, or distribution, coefficient (K_d). The electrical charge of a dissolved constituent in solution significantly influences the partitioning of ions in groundwater. In general, the degree of retardation is proportional to the charge (i.e., charged particles are more likely to be adsorbed than neutral particles, and particles with higher charges will be retained more effectively than particles with a lower charge).

Although attenuation due to sorption was not specifically evaluated in this study, the literature partition coefficients presented in Table 9 provide an indication of the potential for attenuation due to sorption.

TABLE 9
Literature COC Partition Coefficients

Literature Partition Coefficients (mL/g)		
Constituent	Battelle (1989) ^a	Dragun (1988) ^b
Cadmium	14.9	1.3 - 27
Fluoride	0	-
Selenium	5.91	1.2 – 8.6 Se(IV)
Nitrate	0	-
Manganese	16.5	0.2 – 10,000

^a pH range of 5 to 9, <10% adsorbent (clay, organic matter and aluminum oxyhydroxides)

^b K_d ranges for soils and clays.

5.4 Mineral Precipitation

Mineral precipitation and dissolution reactions may control the mobility of constituents in groundwater. Geochemical modeling using PHREEQC (Parkhurst and Appelo, 1999) was conducted to evaluate potential mineral precipitation controls on constituents in groundwater. PHREEQC is an equilibrium mass transfer code developed by the United States Geological Survey (USGS). PHREEQC was used to calculate the aqueous speciation and stability of minerals with respect to dissolved constituents in groundwater. The potential for mineral precipitation was assessed using the saturation index (SI) calculated according to Equation 1.

$$SI = \log (IAP/K_{sp}) \quad (\text{Equation 1})$$

The saturation index is the ratio of the ion activity product (IAP) of a mineral and the solubility product (K_{sp}). An SI greater than zero indicates that the water is supersaturated with respect to a particular mineral phase and, therefore, mineral precipitation may occur. An SI less than zero denotes undersaturation, and the mineral in question will have a general propensity to dissolve. An SI close to zero may be indicative of a solubility control. Following identification of minerals that may be reacting in an aquifer, the likelihood of precipitation/dissolution in the groundwater system is evaluated based on kinetic considerations.

Speciation modeling was conducted for a number of wells along a groundwater flowpath in both the UBZ-2 and UBZ-4 zones to evaluate the potential for mineral precipitation and dissolution reactions to control COC concentrations. Table 10 summarizes the wells for which speciation modeling was conducted over time.

TABLE 10
Speciation Modeling - Monitoring Wells

Aquifer	Wells					
	(listed in order of occurrence along the groundwater flow path)					
UBZ – 2	TW-37 Source Area	TW-22 Source Area	TW-24 Source Area	TW-39	TW-20	TW-54
UBZ – 4	TW-16 Source Area	TW-17 Source Area	TW-50	TW-40 Source Area	TW-26	PW-03

5.5 Cadmium

Speciation modeling results indicate that the precipitation of otavite (CdCO_3) is a possible control on the transport of cadmium.

- **UBZ-2** – Otavite saturation indices for the UBZ-2 wells are shown in Figure 11. The otavite saturation indices for the source area wells (i.e., TW-37, TW-22, and TW-24) are often between -0.5 and 0.5, indicating equilibrium conditions. These results suggest that close to the source, otavite is likely precipitating thereby retarding the advancement of the cadmium plume. The downgradient wells are undersaturated with respect to otavite.
- **UBZ-4** – Otavite saturation indices for the UBZ-4 wells are shown in Figure 12. The otavite saturation indices for the source area wells (i.e., TW-16 and TW-40) are equal to or greater than 0.5, indicating equilibrium or supersaturated conditions. These results suggest that close to the source, otavite is likely precipitating thereby retarding the advancement of the cadmium plume. The downgradient wells are undersaturated with respect to otavite.

Both chloride and cadmium concentrations are currently increasing in well TW-37. Recent increases in cadmium concentrations at this well may be attributed to dissolution of previously precipitated otavite, as opposed to release from the former Underflow Solids Ponds source. Appendix E of the second five year report (Golder, 2008) discussed the potential for increases in groundwater chloride concentrations to increase the solubility of otavite due to the formation of cadmium-chloride complexes. Figure 13 shows the solubility curve for otavite assuming two different chloride concentrations. The lower curve was modeled assuming the groundwater quality measured at TW-37 in June 1999 and a chloride concentration of 25 mg/L. The upper curve was generated using the May 2009 groundwater quality for TW-37 and a chloride concentration of 508 mg/L. As the concentration of chloride increases, the amount of cadmium complexed with chloride increases and thus the concentration of cadmium in groundwater increases.

5.6 Manganese

Manganese mobility in groundwater is reduced under oxidizing conditions where manganese concentrations can be reduced by the precipitation of manganese oxide, oxyhydroxides, and carbonates. Manganese concentrations are currently stable in most UBZ-2 and UBZ-4 wells. Rhodochrosite (MnCO_3)

saturation indices over time for the UBZ-2 and UBZ-4 wells are shown in Figures 14 and 15. Manganese concentrations in TW-22 and TW-37 are currently stable at approximately 0.7 to 0.8 mg/L and are likely controlled by the precipitation of rhodochrosite. The speciation model results indicate that the groundwater at these wells is near equilibrium with respect to rhodochrosite. Within the UBZ-4, rhodochrosite is identified as a likely control in areas where manganese concentrations are highest (i.e., TW-17, TW-50, and TW-26).

5.7 Fluoride

Fluoride mobility in groundwater may be reduced by the precipitation of fluorite (CaF_2). Fluoride concentrations in the wells modeled in UBZ-2 are steady or decreasing (TW-37) with the exception of TW-39 which demonstrates an increasing fluoride concentration trend. Fluorite saturation indices for the UBZ-2 wells are shown in Figure 16. Fluorite is supersaturated in TW-37, the most upgradient source well. In the two remaining source wells (TW-22 and TW-24), speciation modeling results indicate equilibrium with respect to fluorite. The downgradient wells (TW-39, TW-20 and TW-54) also indicate equilibrium conditions with respect to fluorite. These results suggest that precipitation of fluorite is a control on fluoride mobility. Supersaturation at the most upgradient well may be indicative of slower reaction kinetics resulting in some transport prior to precipitation.

Fluorite saturation indices for the UBZ-4 wells are shown in Figure 17. In UBZ-4, fluoride concentrations are currently decreasing in the source area wells, while the other wells show steady levels of fluoride. Precipitation of fluorite in the source areas (TW-16 and TW-40) is a likely control on fluoride concentrations.

5.8 Selenium

Selenium is mobile under the groundwater conditions at the Monsanto site and selenium appears to be transported conservatively. The chemical hydrographs for the UBZ-2 wells show the arrival of concentration peaks in downgradient wells at the estimated rate of groundwater flow (Figures 4b and 7b).

5.9 Nitrate

Nitrate is transported conservatively in groundwater. The principal attenuation mechanism is denitrification under reducing conditions. This condition is not met at the Monsanto site and nitrate is transported in groundwater with no retardation.

5.10 Summary

Table 11 presents a summary of the likely attenuation mechanisms present at the Monsanto site for the COCs.

TABLE 11
Main Attenuation Mechanisms At The Monsanto Site

Parameter	Attenuation Mechanism		
	Mineral Precipitation	Sorption	Dispersion
Cadmium	Otavite (CdCO_3)	Possibly manganese oxyhydroxides and calcite.	Yes
Fluoride	Fluorite (CaF_2)		Yes
Manganese	Rhodochrosite (MnCO_3)	None	Yes
Nitrate	None	None	Yes
Selenium	None	None	Yes

6.0 CONCLUSION

The objective of the current evaluation was to review the Monsanto groundwater quality data to determine the effectiveness of natural attenuation for cadmium, manganese, fluoride, selenium, and nitrate.

The evaluation indicates that natural attenuation due to secondary mineral precipitation, dispersion and possible adsorption is occurring for cadmium, fluoride, and manganese. Otavite, fluorite, and rhodochrosite, respectively, have been identified as the most likely mineral phase controls for these constituents in the source areas. The only natural attenuation mechanism for nitrate and selenium is dispersion, and this has resulted in reduction of nitrate and selenium concentrations for wells located downgradient of the source area wells, especially for the UBZ-4. Greater dispersion within the UBZ-4 is likely attributed to greater lateral dispersion than within the UBZ-2 and the effects of pumping.

Application of magnesium chloride dust suppression chemicals may have resulted in increased chloride concentrations in some locations on the Plant site as a result of runoff and potential infiltration. The possible effects of dust suppressant application are most evident at TW-37. At this well, the increased chloride concentrations in groundwater have likely resulted in dissolution and re-mobilized previously precipitated cadmium carbonate (otavite) from the source areas.

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FIGURES

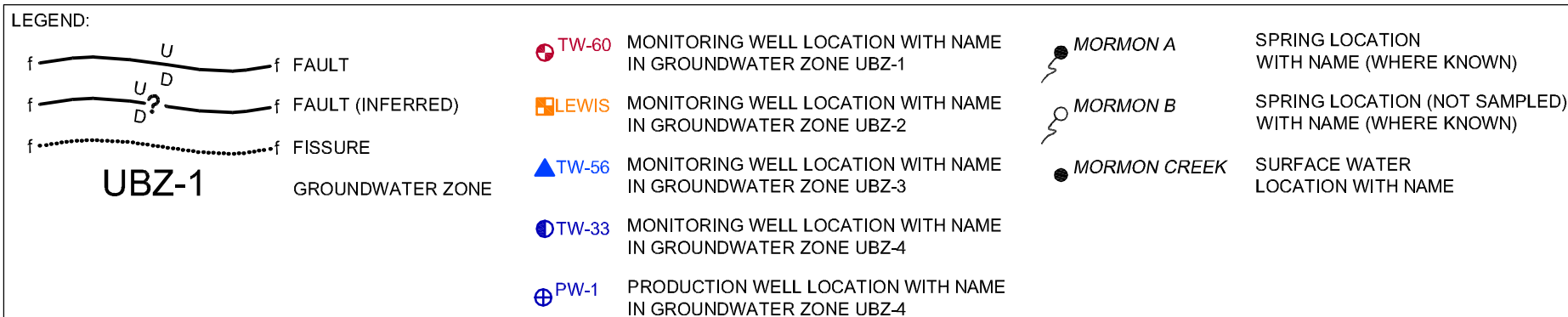
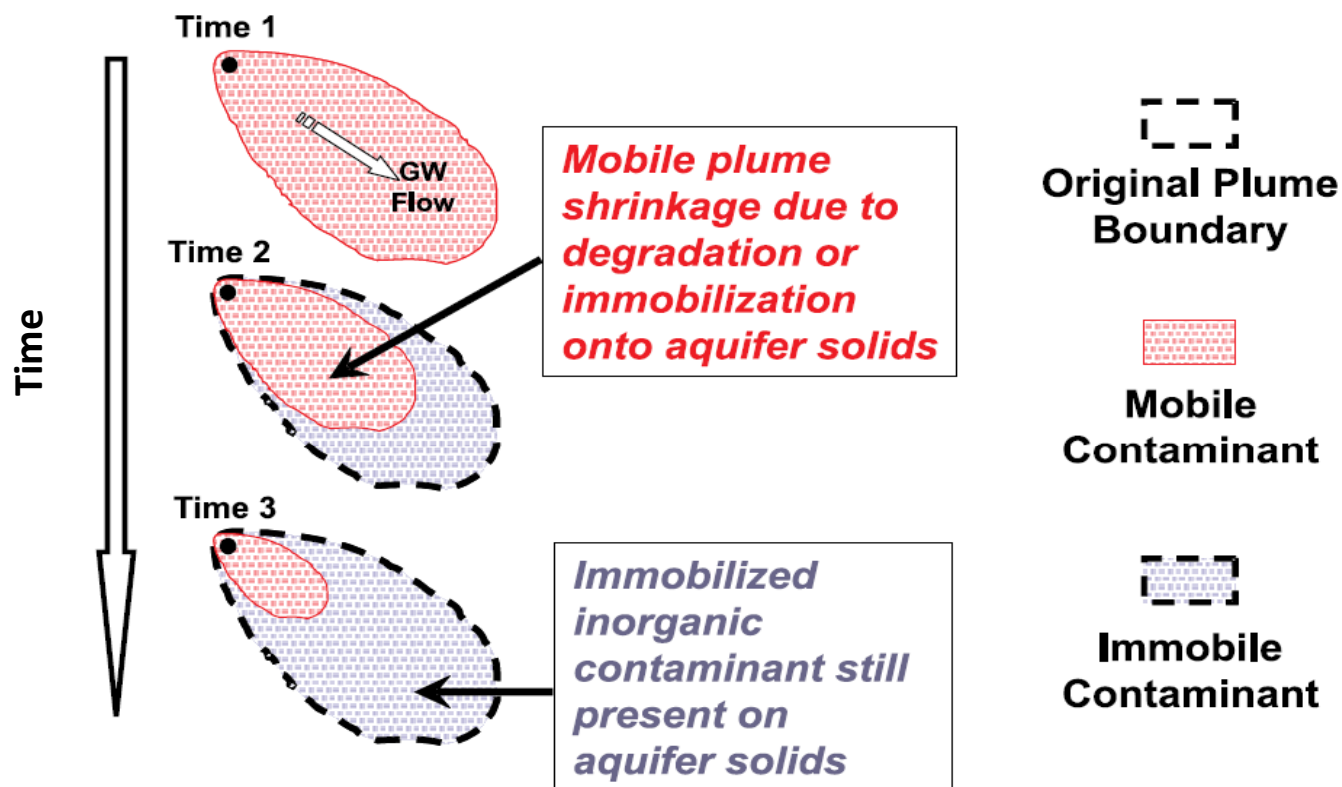


FIGURE 1

**LOCATION OF SPRINGS AND WELLS
IN THE UPPER BASALT ZONE**

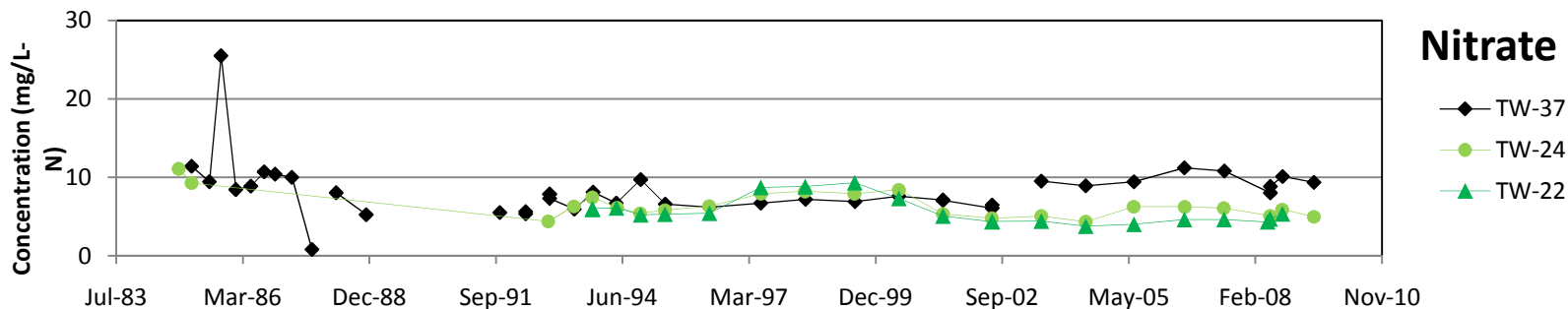
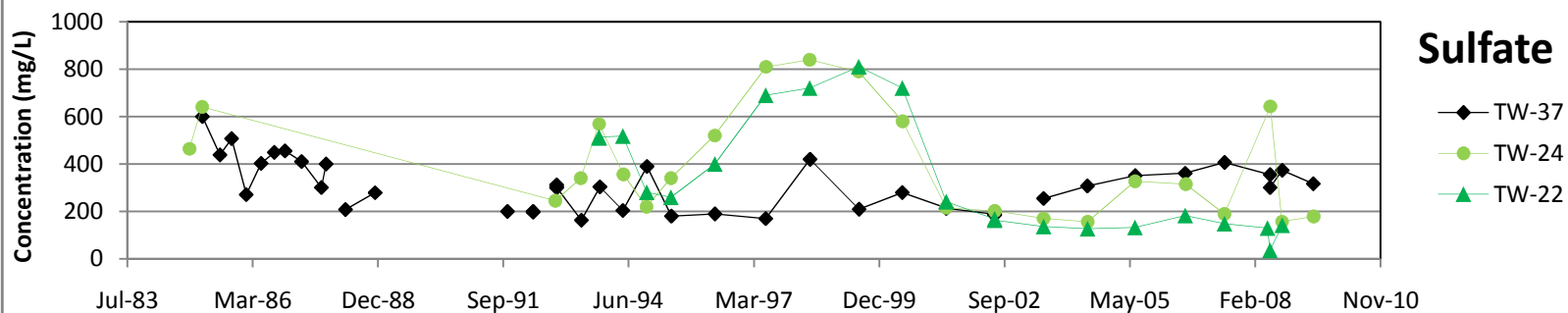
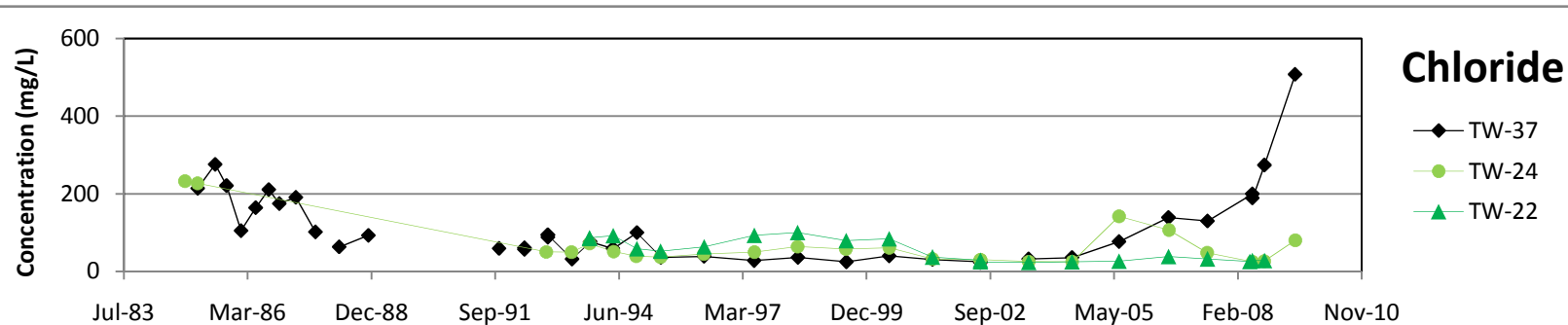
EVALUATION OF NATURAL ATTENUATION CONTROLS



Reproduced from EPA, 2007



Title		Evolution of inorganic contaminant plume (EPA, 2007)		Drawn	FV
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	CR
Client Name		Monsanto		Reviewed	DB
		Date	November 2009	FIGURE 2	



Title

UBZ-2 Source Wells - Cl, SO4 and NO3

Project Name

Monsanto Soda Springs - Natural Attenuation

Project No.

913-1101.605

Client Name

Monsanto

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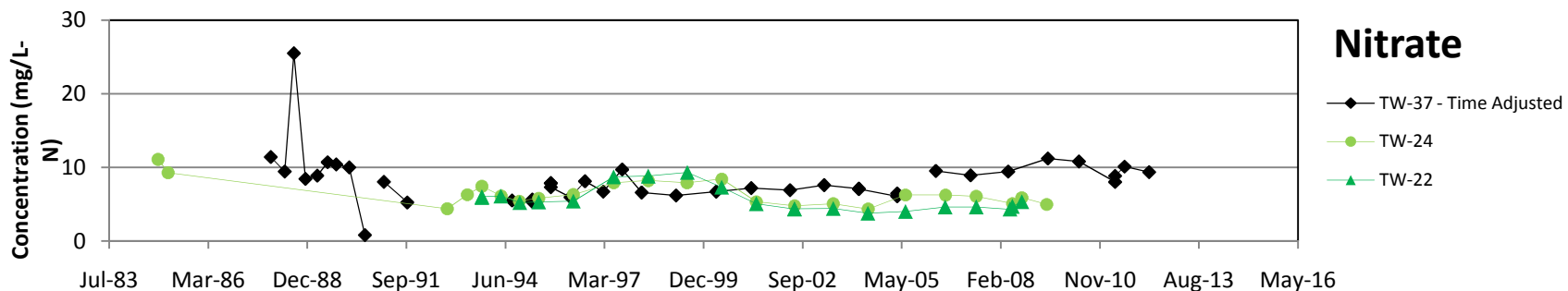
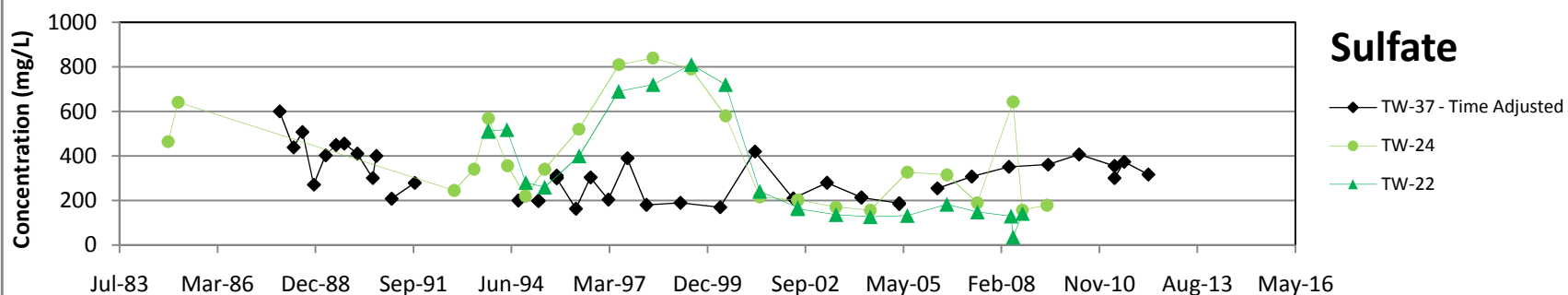
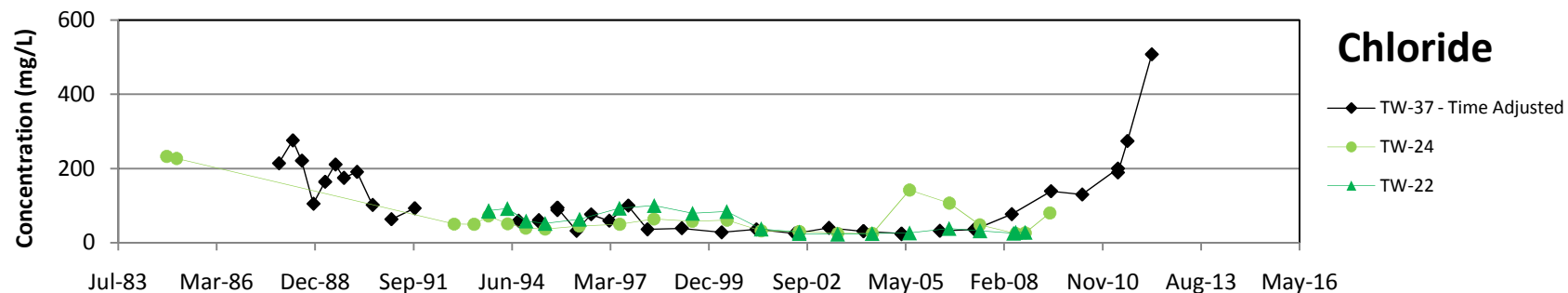
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FIGURE

3a



Title **UBZ-2 Source Wells - Cl, SO4 and NO3 (Time Adjusted)**

Project Name **Monsanto Soda Springs - Natural Attenuation**

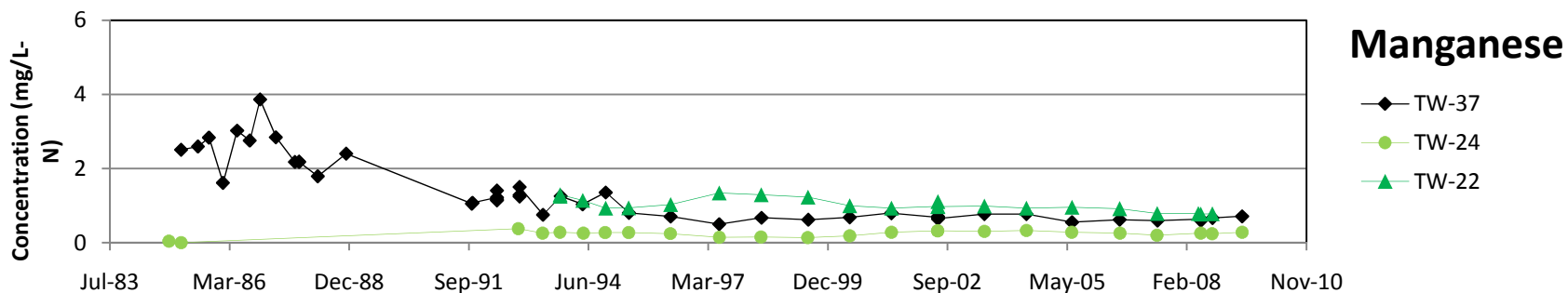
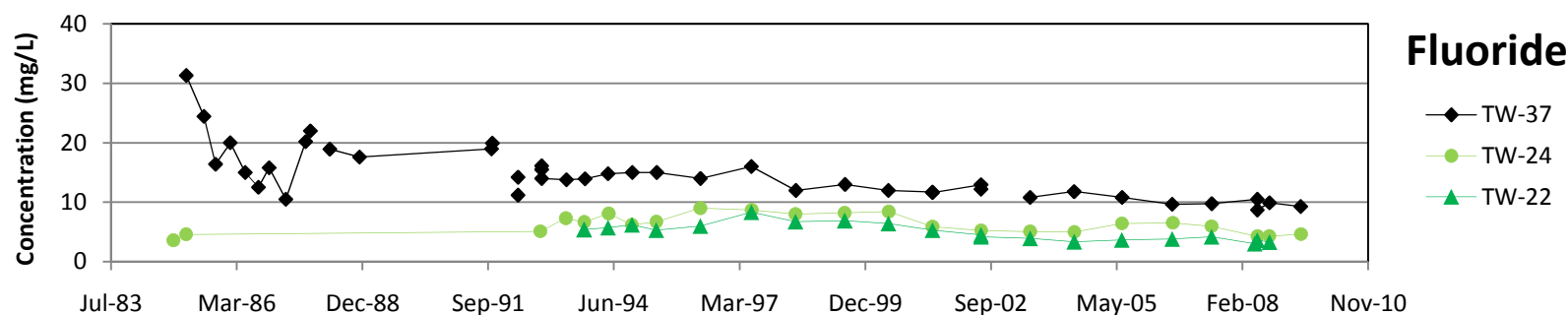
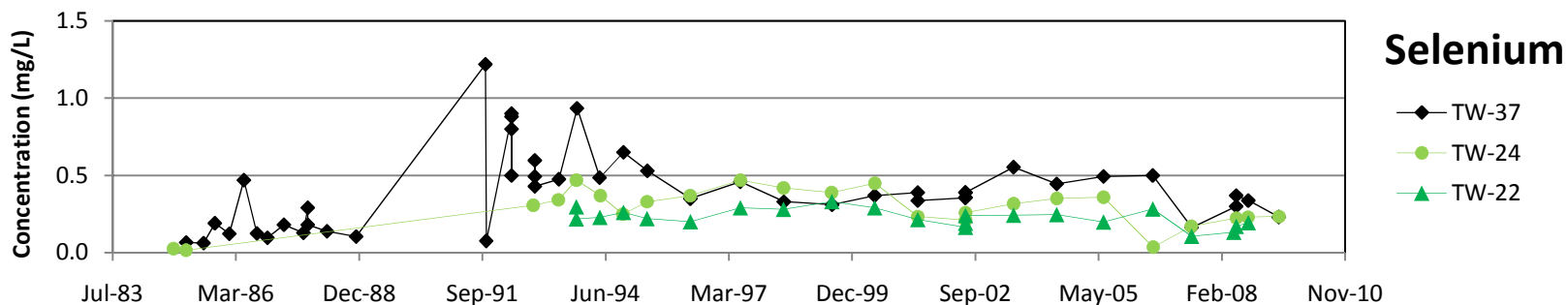
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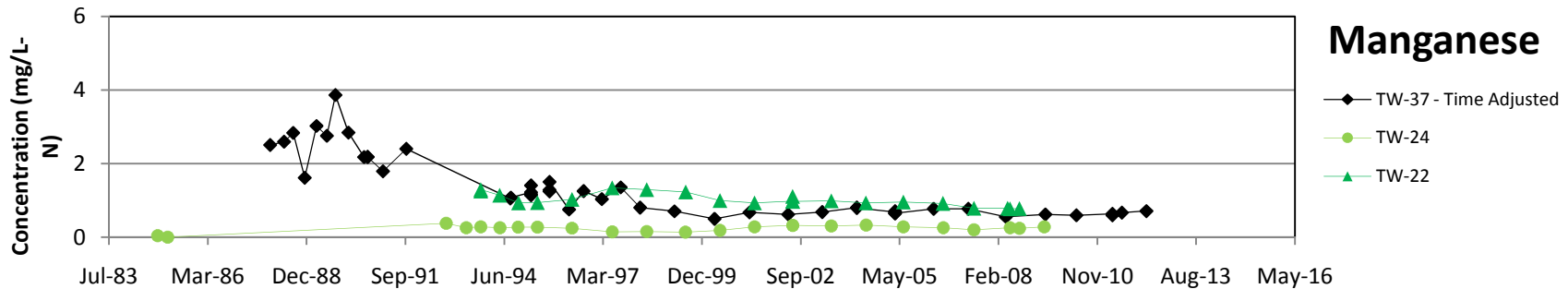
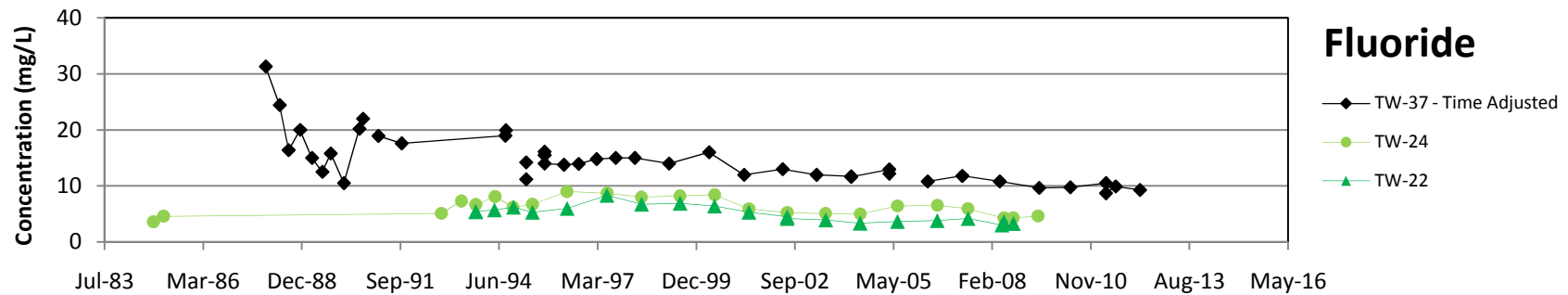
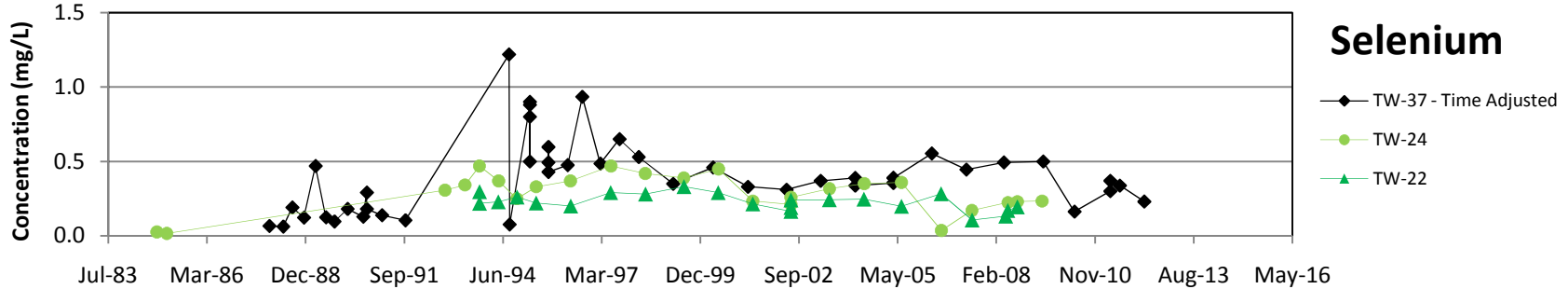
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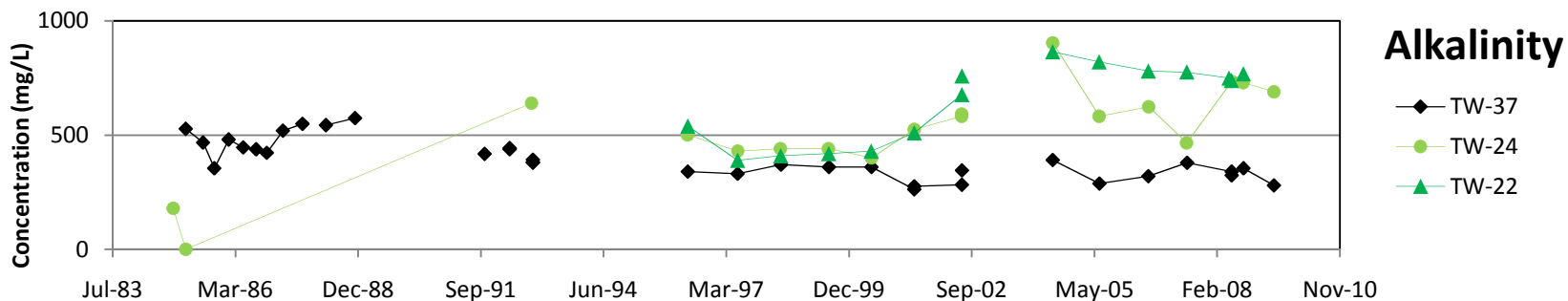
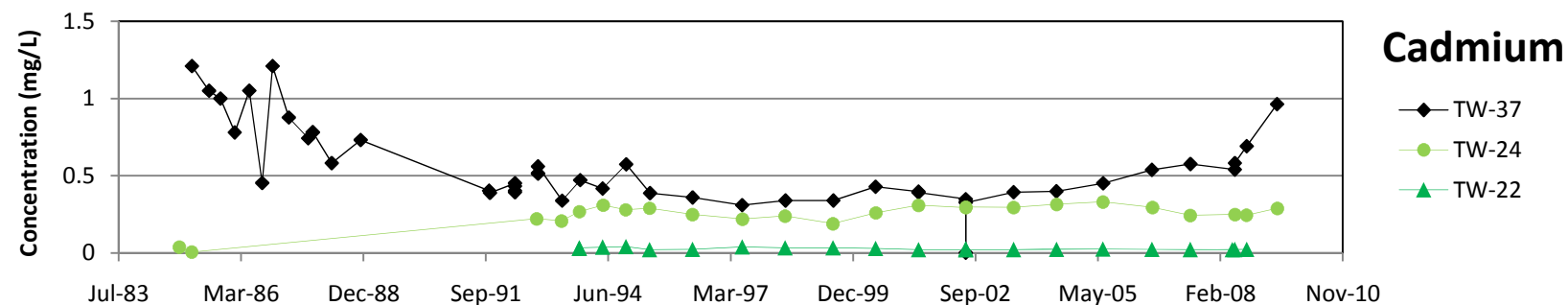
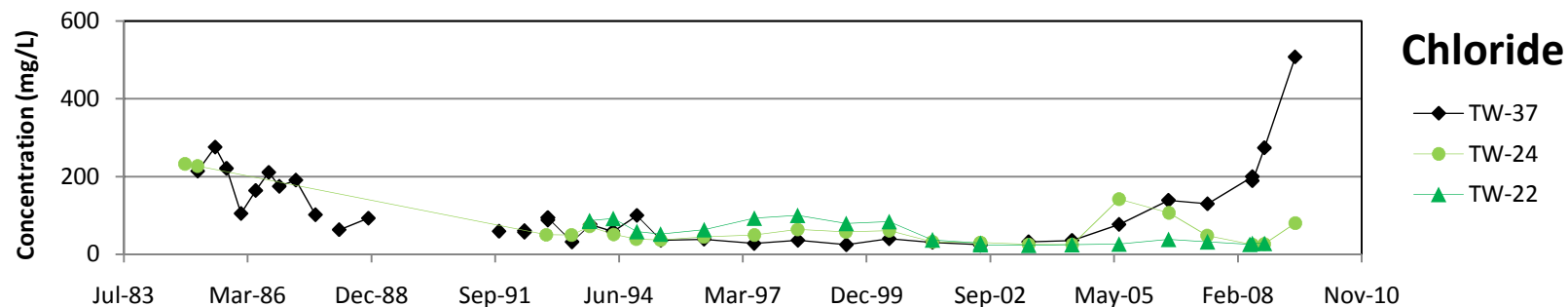
FIGURE **3b**



Title		UBZ-2 Source Wells - Se, F and Mn		Drawn	CR
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	FV
Client Name		Monsanto		Reviewed	DB
		Project No.	913-1101.605	FIGURE 4a	
		Date	November 2009		



Title		UBZ-2 Source Wells - Se, F and Mn (Time Adjusted)		Drawn	CR
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	FV
Client Name		Monsanto		Reviewed	DB
		Project No.	913-1101.605	FIGURE 4b	
		Date	November 2009		



Title: UBZ-2 Source Wells - Cl, Cd and Alkalinity

Project Name: Monsanto Soda Springs - Natural Attenuation

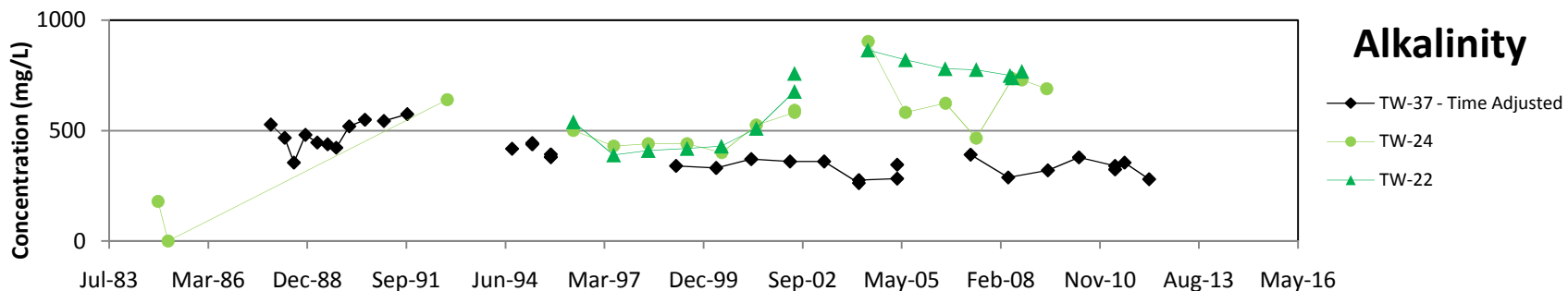
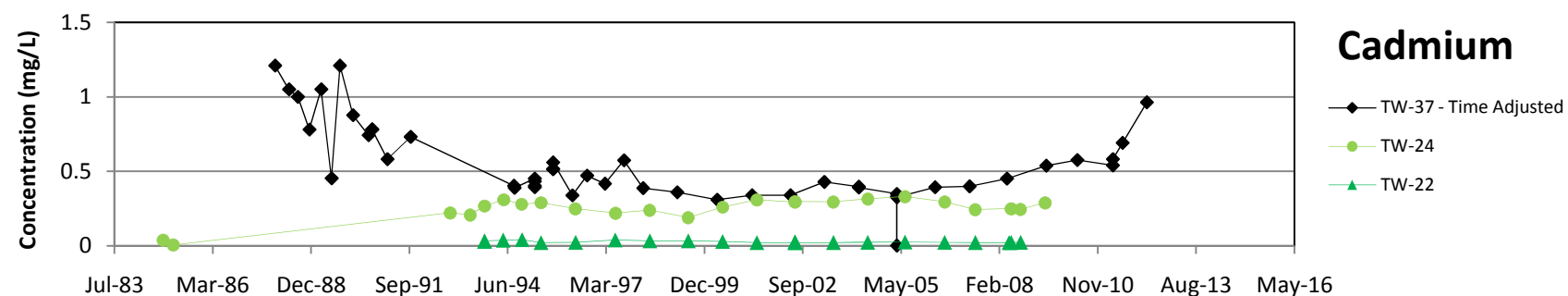
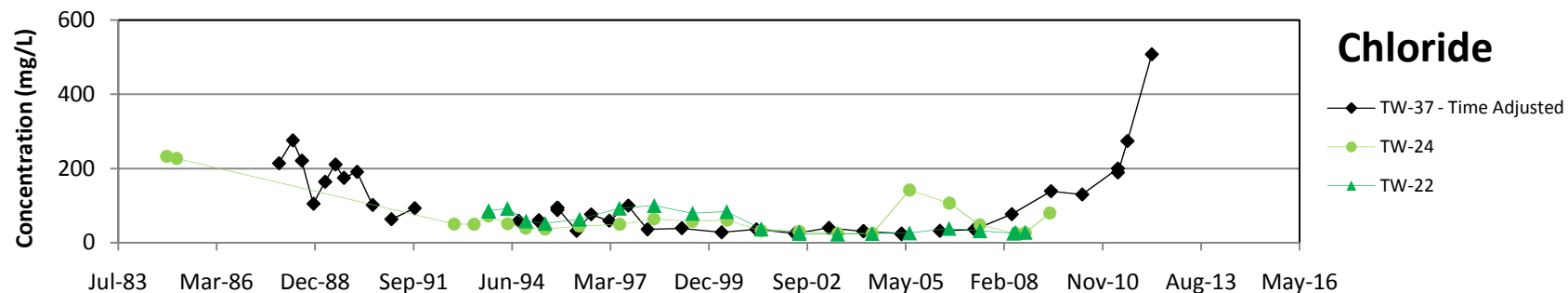
Project No.: 913-1101.605

Client Name: Monsanto

Date: November 2009

Drawn	CR
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Reviewed	DB

FIGURE 5a



Title: UBZ-2 Source Wells - Cl, Cd and Alkalinity (Time Adjusted)

Project Name: Monsanto Soda Springs - Natural Attenuation

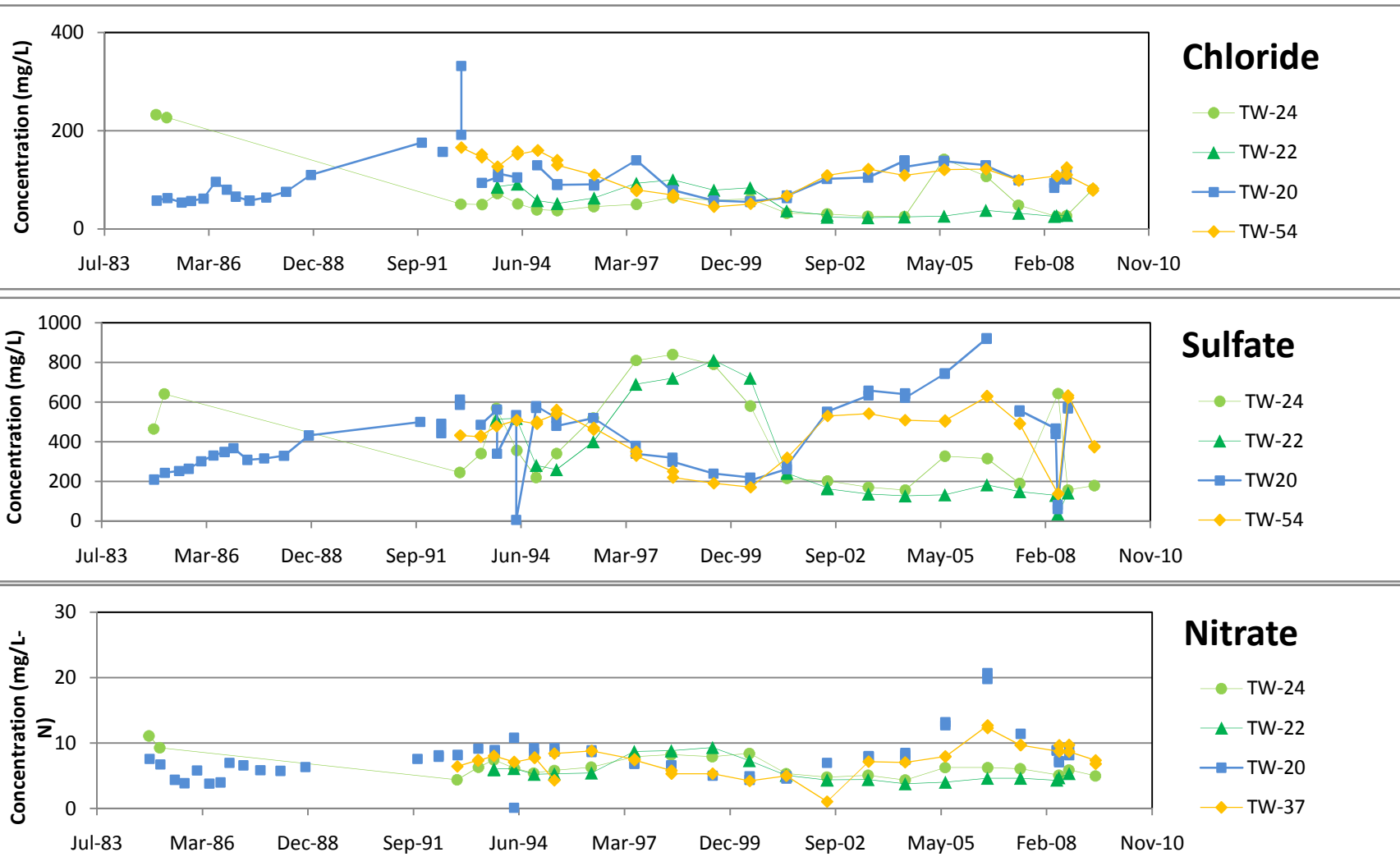
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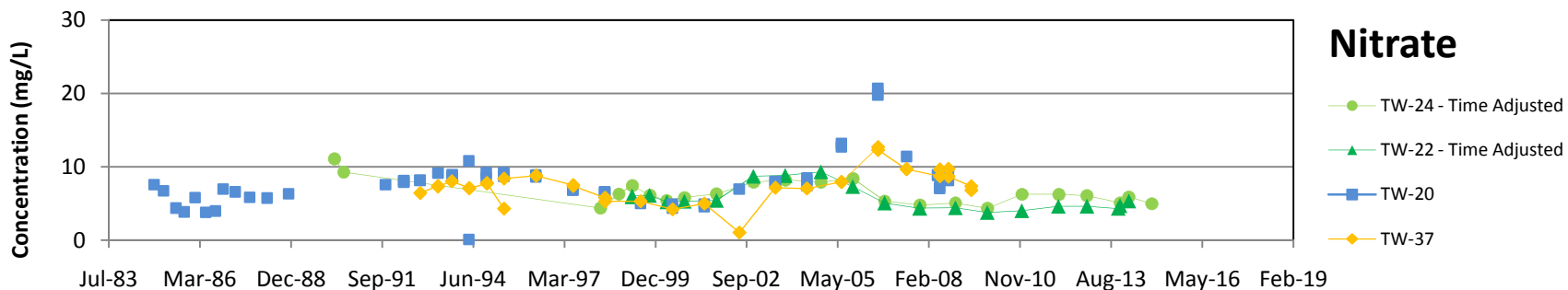
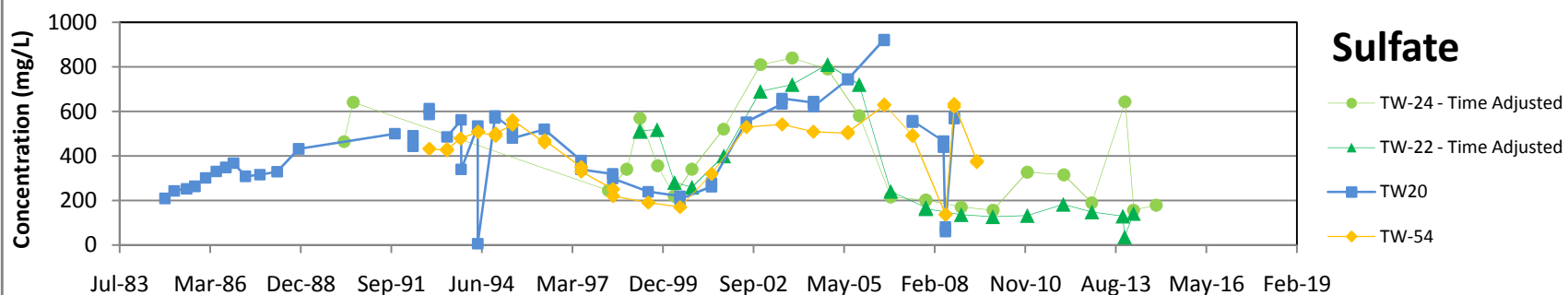
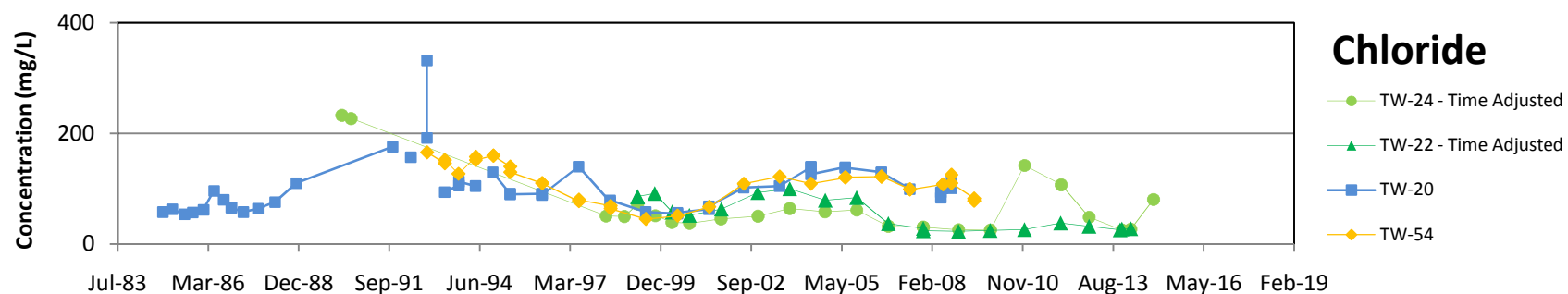
Date: November 2009

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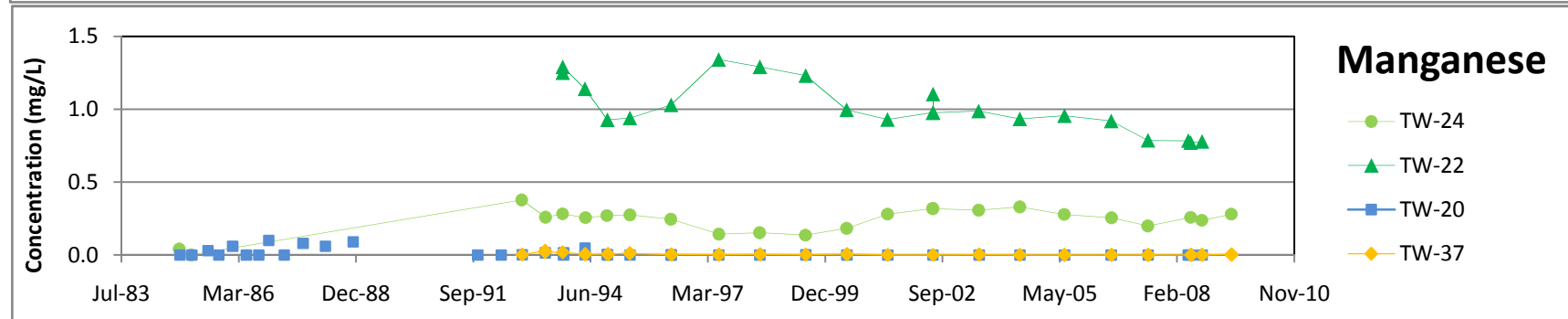
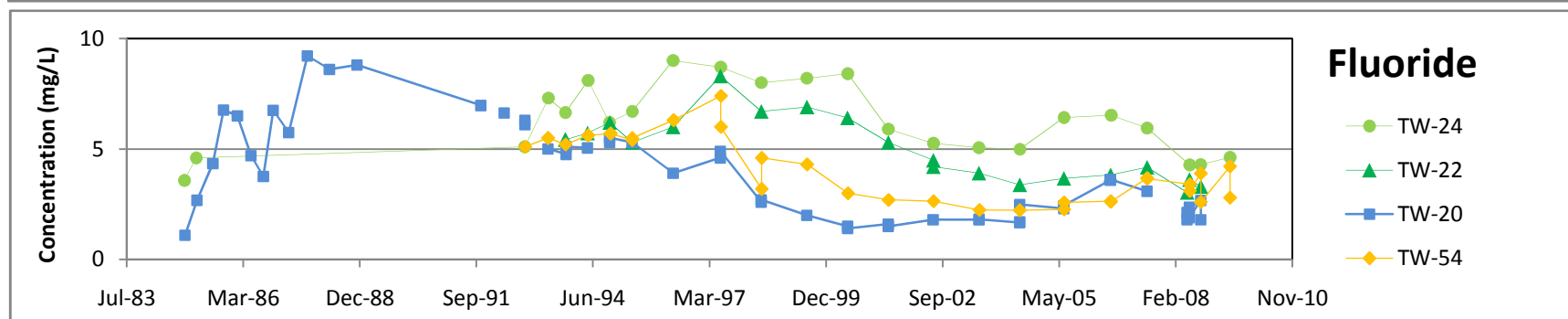
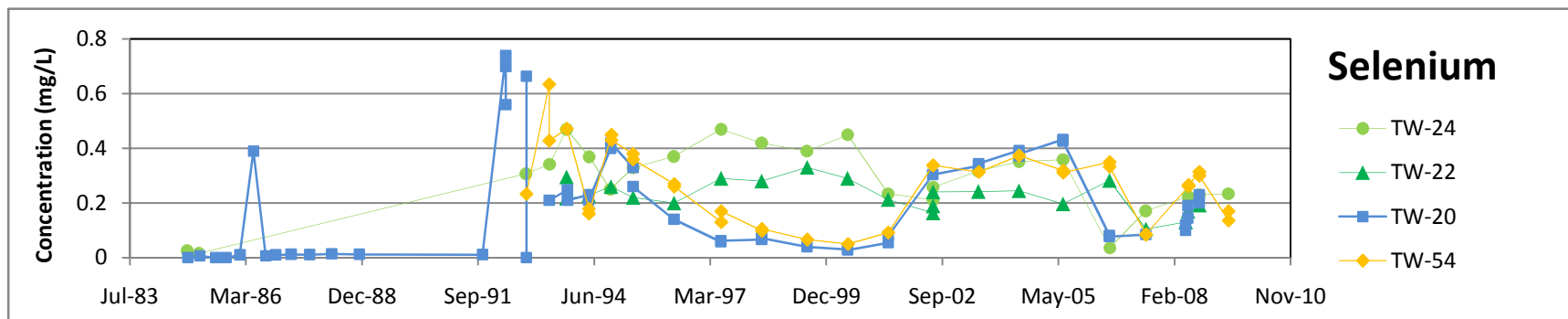
FIGURE 5b



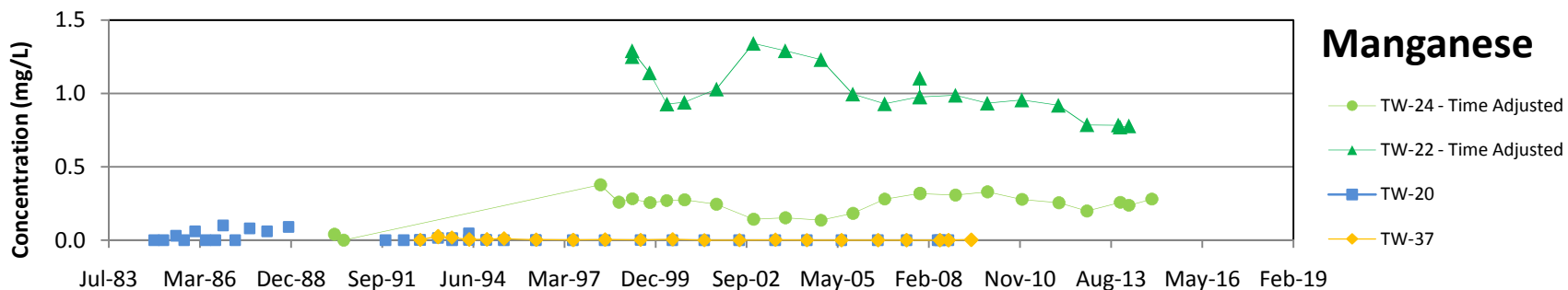
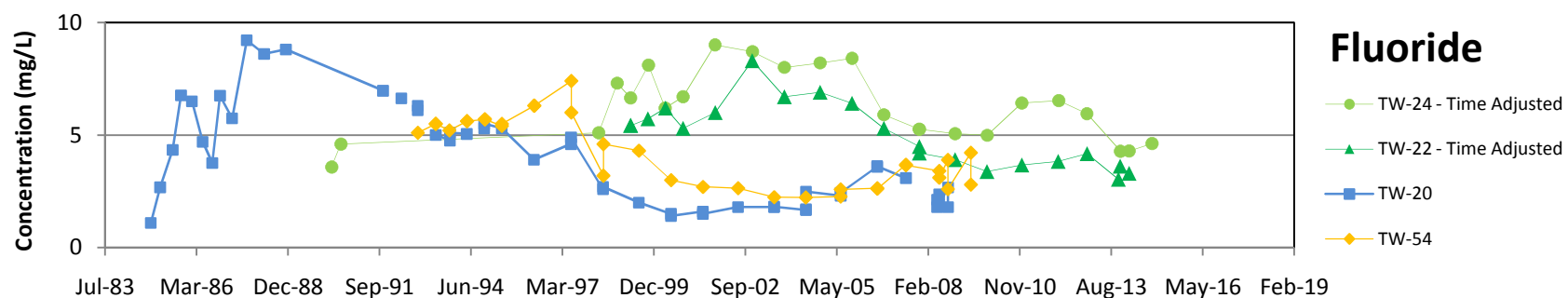
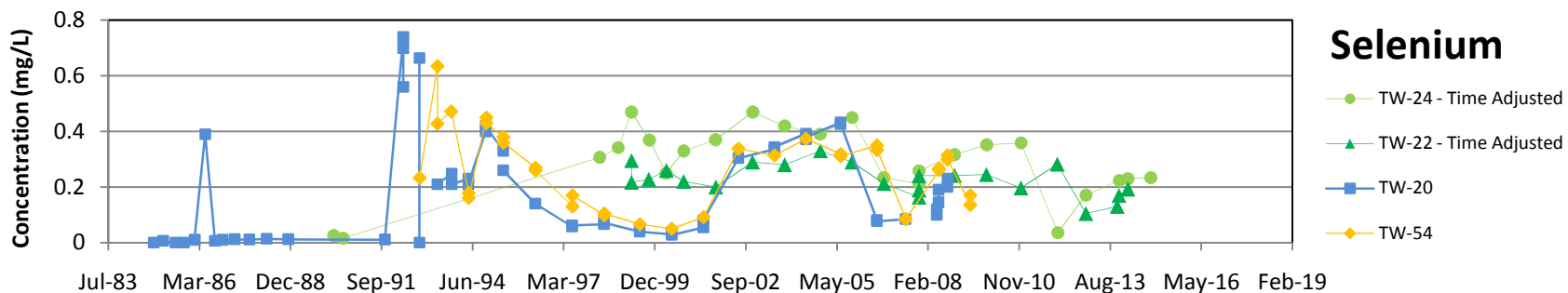
Title		UBZ-2 Wells - Cl, SO4 and NO3		Drawn	CR
				Checked	FV
Project Name	Monsanto Soda Springs - Natural Attenuation	Project No.	913-1101.605	Reviewed	DB
Client Name	Monsanto	Date	November 2009	FIGURE 6a	



Title		UBZ-2 Wells - Cl, SO4 and NO3 (Time Adjusted)		Drawn	CR
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	FV
Client Name		Monsanto		Reviewed	DB
		Project No.	913-1101.605	FIGURE 6b	
		Date	November 2009		



	Title		UBZ-2 Wells - Se, F and Mn	Drawn	CR
	Project Name		Monsanto Soda Springs - Natural Attenuation	Checked	FV
	Client Name		Monsanto	Reviewed	DB
	Project No.		913-1101.605	FIGURE 7a	
	Date		November 2009		



Title

UBZ-2 Wells - Se, F and Mn (Time Adjusted)

Project Name

Monsanto Soda Springs - Natural Attenuation

Project No.

913-1101.605

Client Name

Monsanto

Date

November 2009

Drawn

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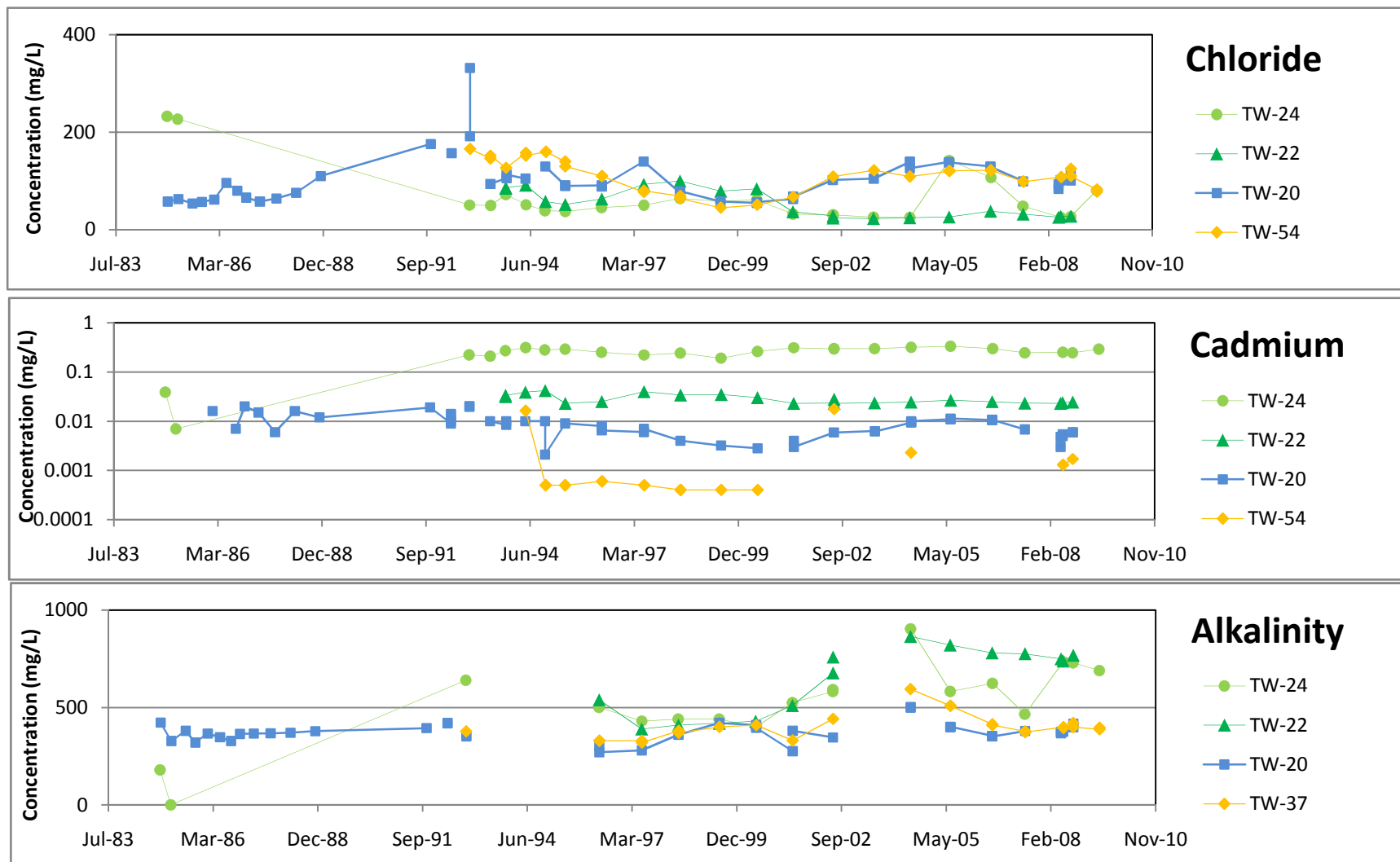
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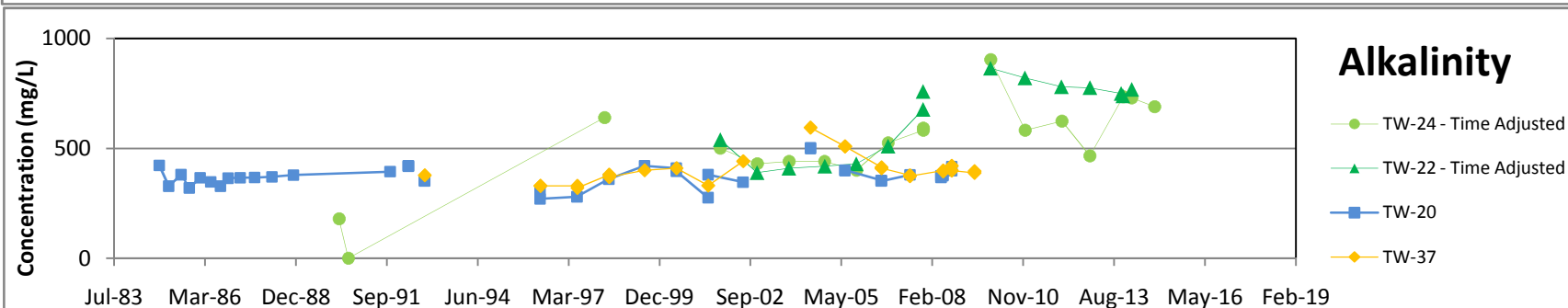
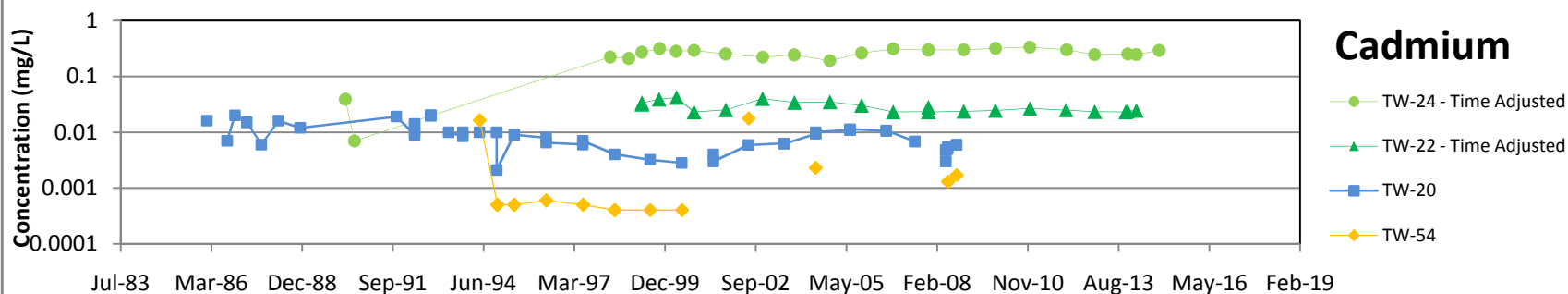
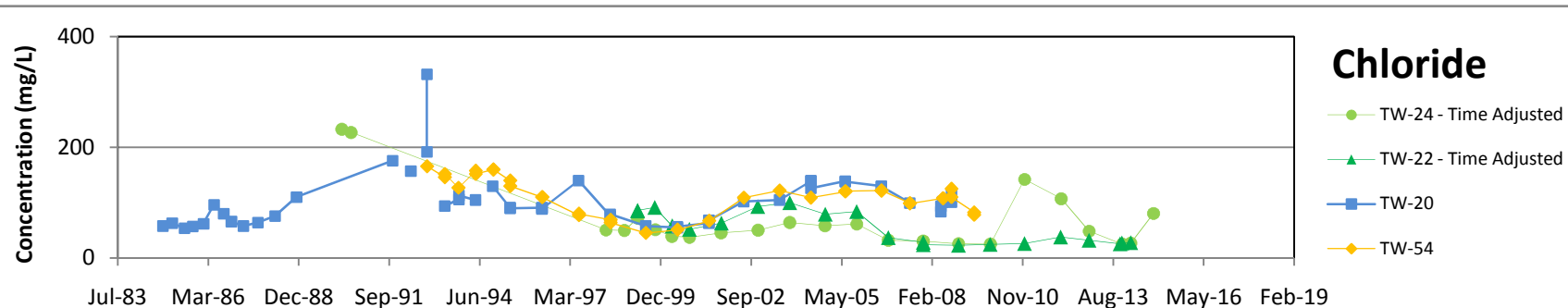
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FIGURE

7b



Title		UBZ-2 Wells - Cl, Cd and Alkalinity		Drawn	CR
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	FV
Client Name		Monsanto		Reviewed	DB
		Project No.	913-1101.605	FIGURE 8a	
		Date	November 2009		



Title **UBZ-2 Wells - Cl, Cd and Alkalinity (Time Adjusted)**

Project Name **Monsanto Soda Springs - Natural Attenuation**

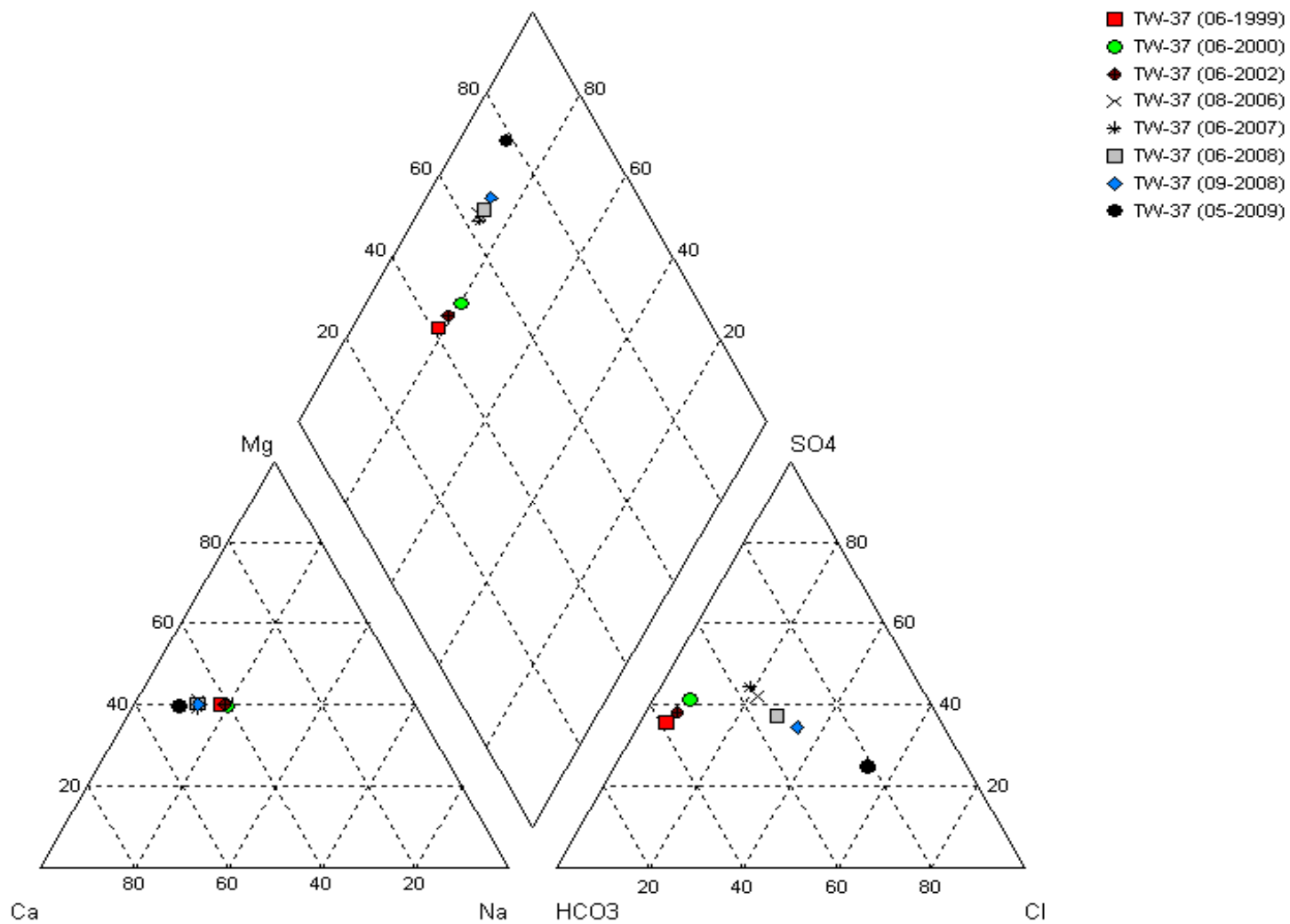
Project No. **913-1101.605**

Client Name **Monsanto**

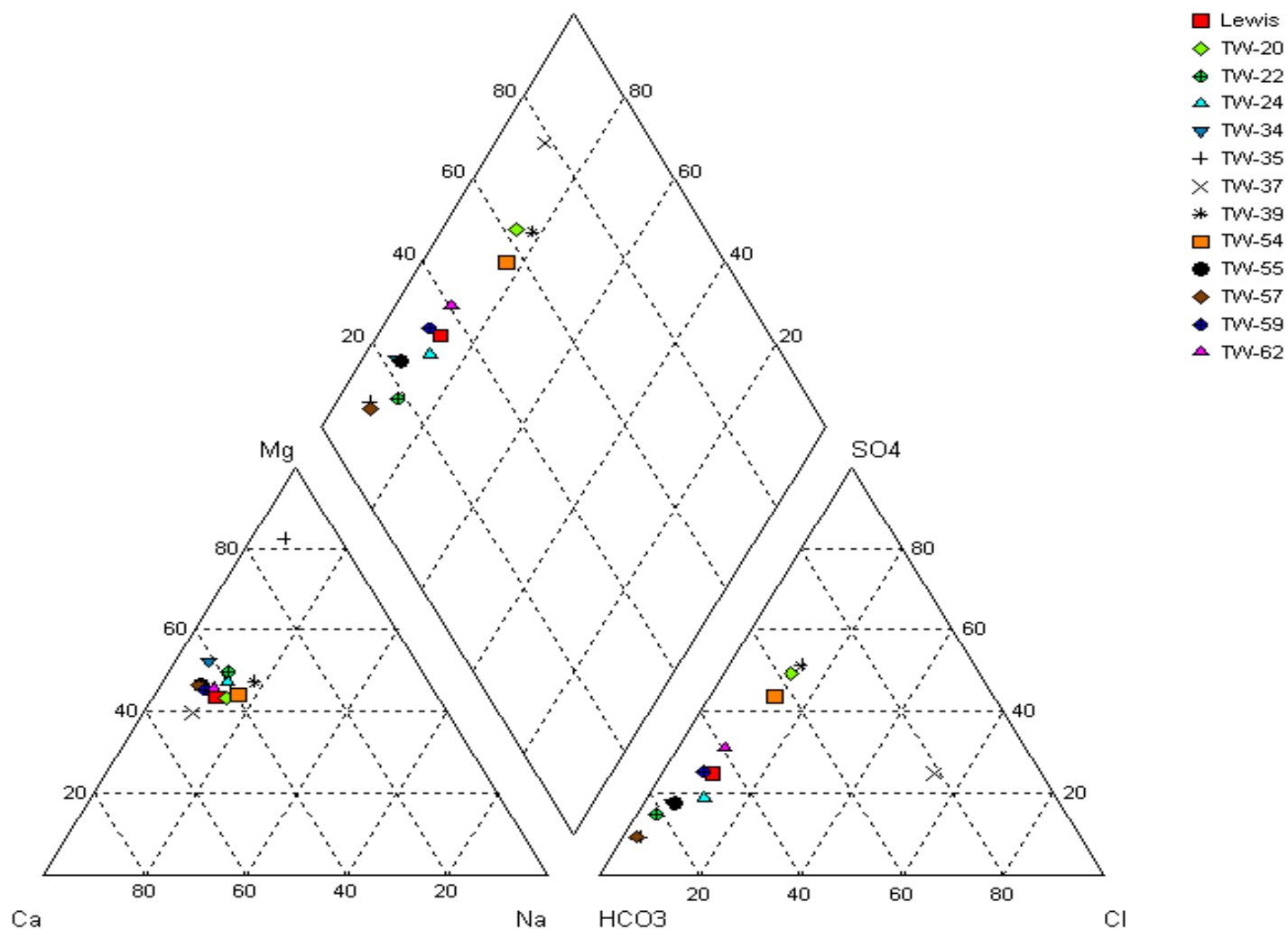
Date **November 2009**

Drawn	CR
Checked	FV
Reviewed	DB

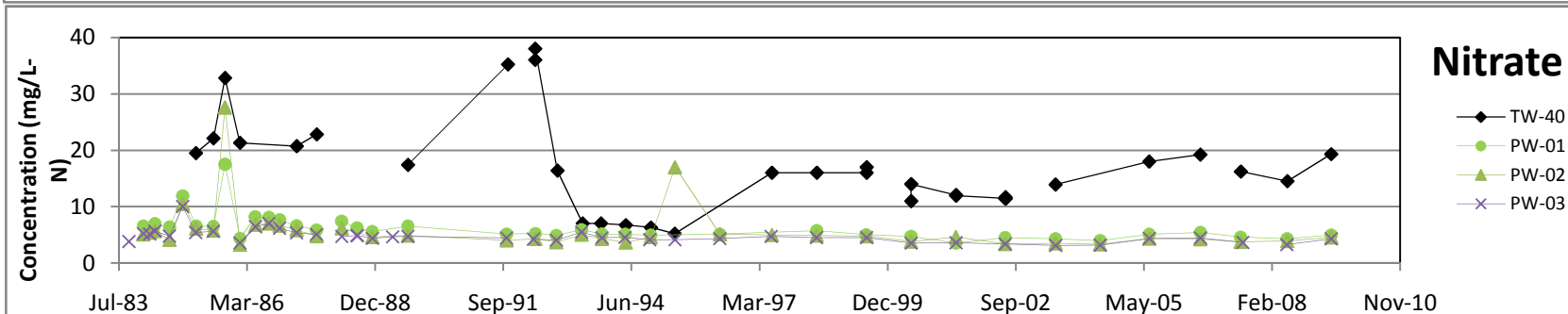
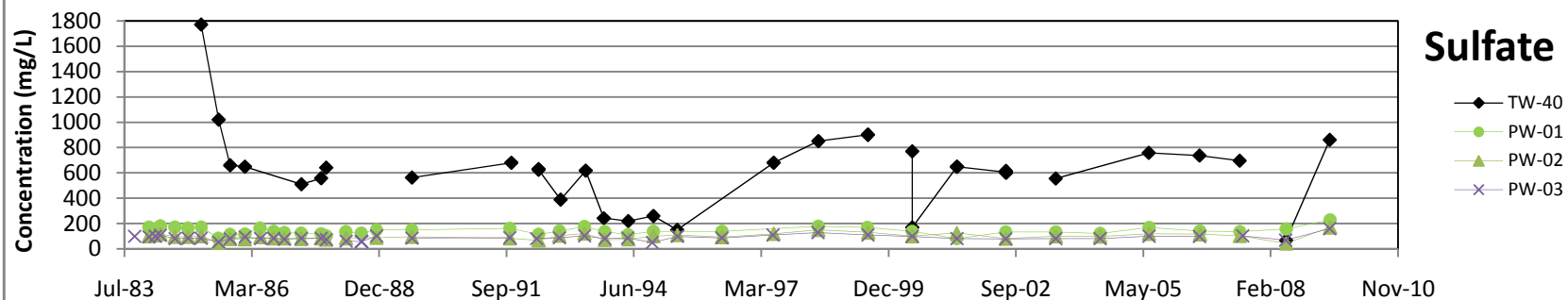
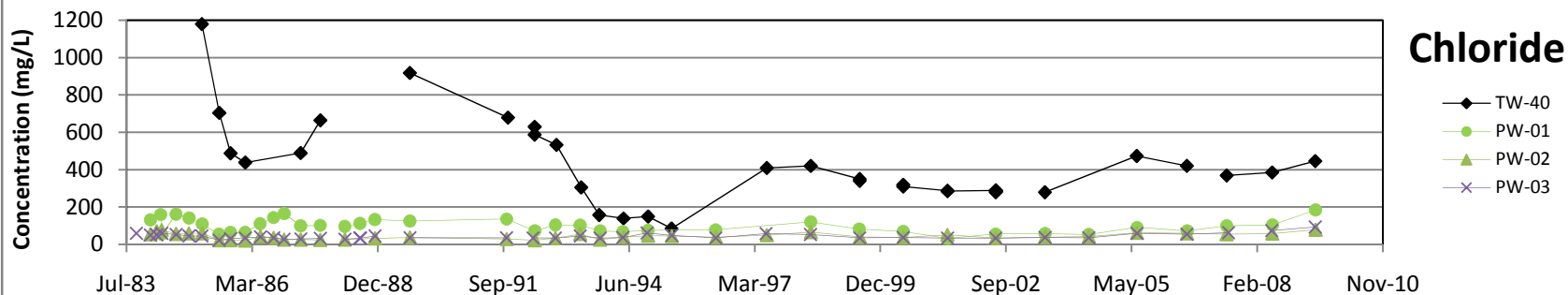
FIGURE **8b**



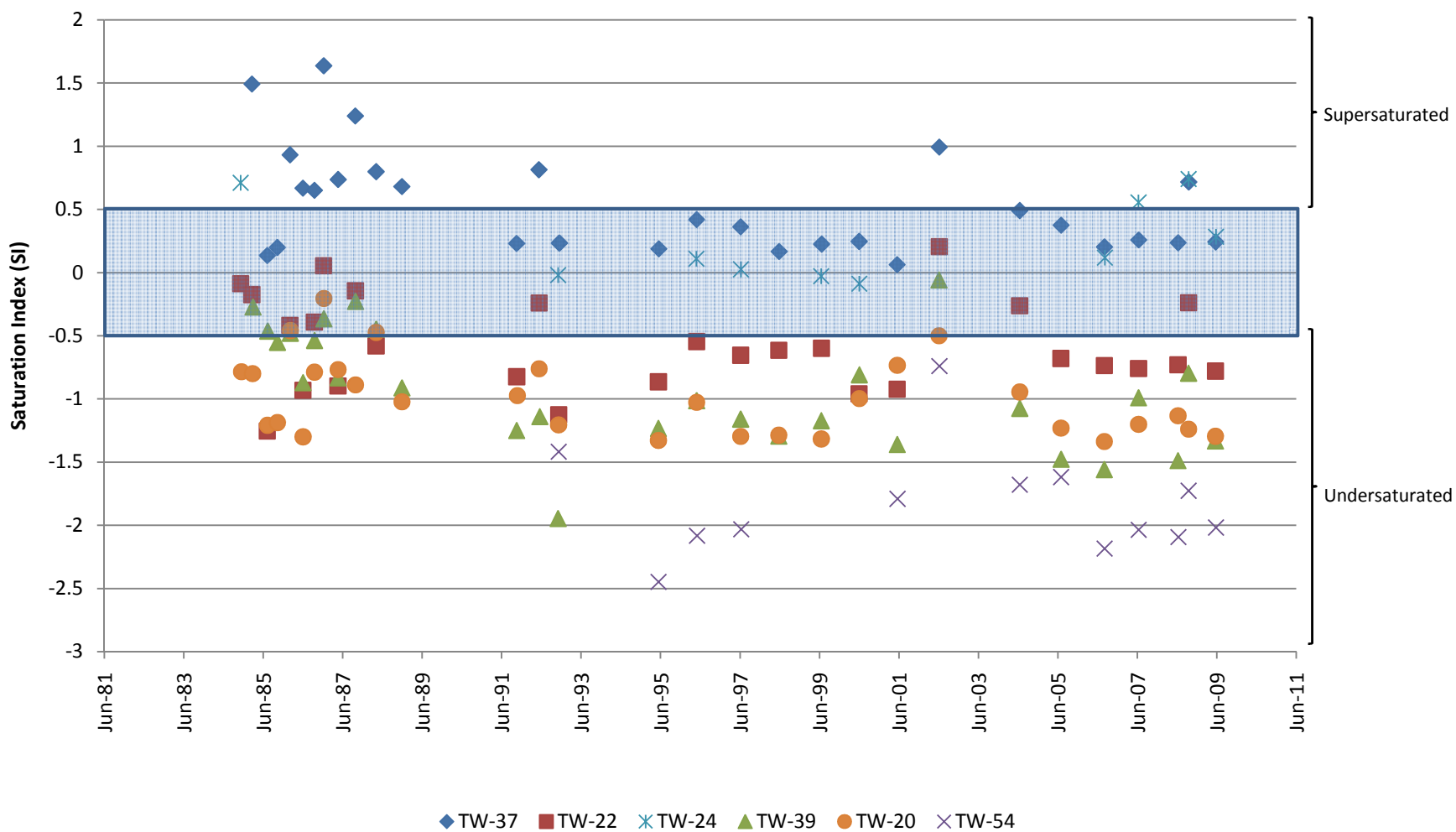
Title			Piper plot - TW-37 (1999 - 2009)		Drawn	FV
					Checked	CR
Project Name	Monsanto Soda Springs - Natural Attenuation		Project No.	913-1101.605	Reviewed	DB
Client Name	Monsanto		Date	November 2009	FIGURE 9a	



Title		Piper plot UBZ-2 wells (2009)		Drawn	FV
				Checked	CR
Project Name	Monsanto Soda Springs - Natural Attenuation	Project No.	913-1101.605	Reviewed	DB
Client Name	Monsanto	Date	November 2009	FIGURE 9b	



Title		UBZ-4 Source Wells - Cl, SO4 and NO3		Drawn	FV
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	DB
Client Name		Monsanto		Reviewed	DB
		Project No.	913-1101.605	FIGURE 10	
		Date	November 2009		



Title

UBZ-2 Otavite (CdCO3) SI vs time

Project Name

Monsanto Soda Springs - Natural Attenuation

Project No.

913-1101.605

Client Name

Monsanto

Date

November 2009

Drawn

FV

Checked

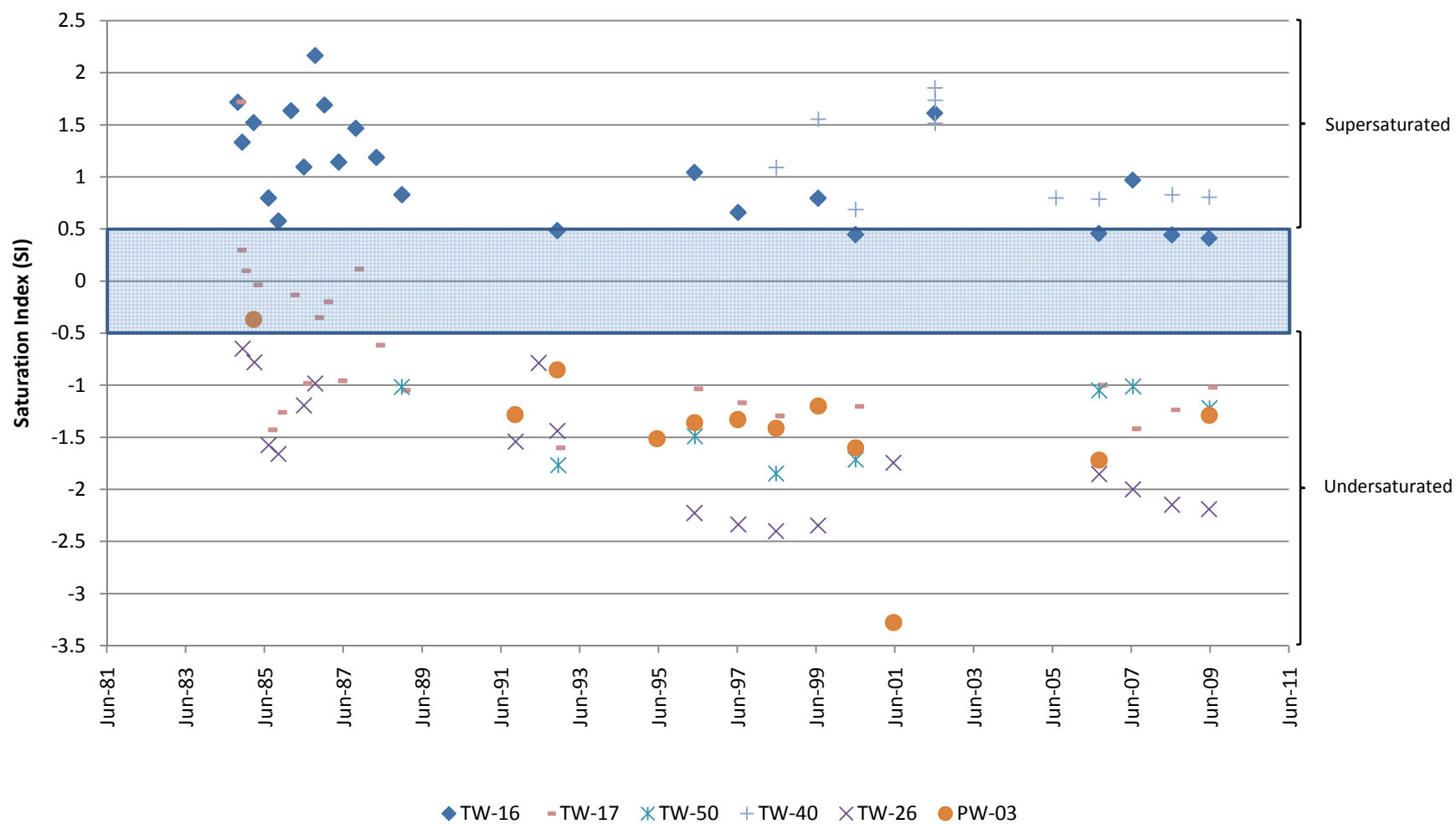
CR

Reviewed

DB

FIGURE

11



Title

UBZ-4 Otavite (CdCO_3) SI vs time

Project Name

Monsanto Soda Springs - Natural Attenuation

Project No.

913-1101.605

Client Name

Monsanto

Date

November 2009

Drawn

FV

Checked

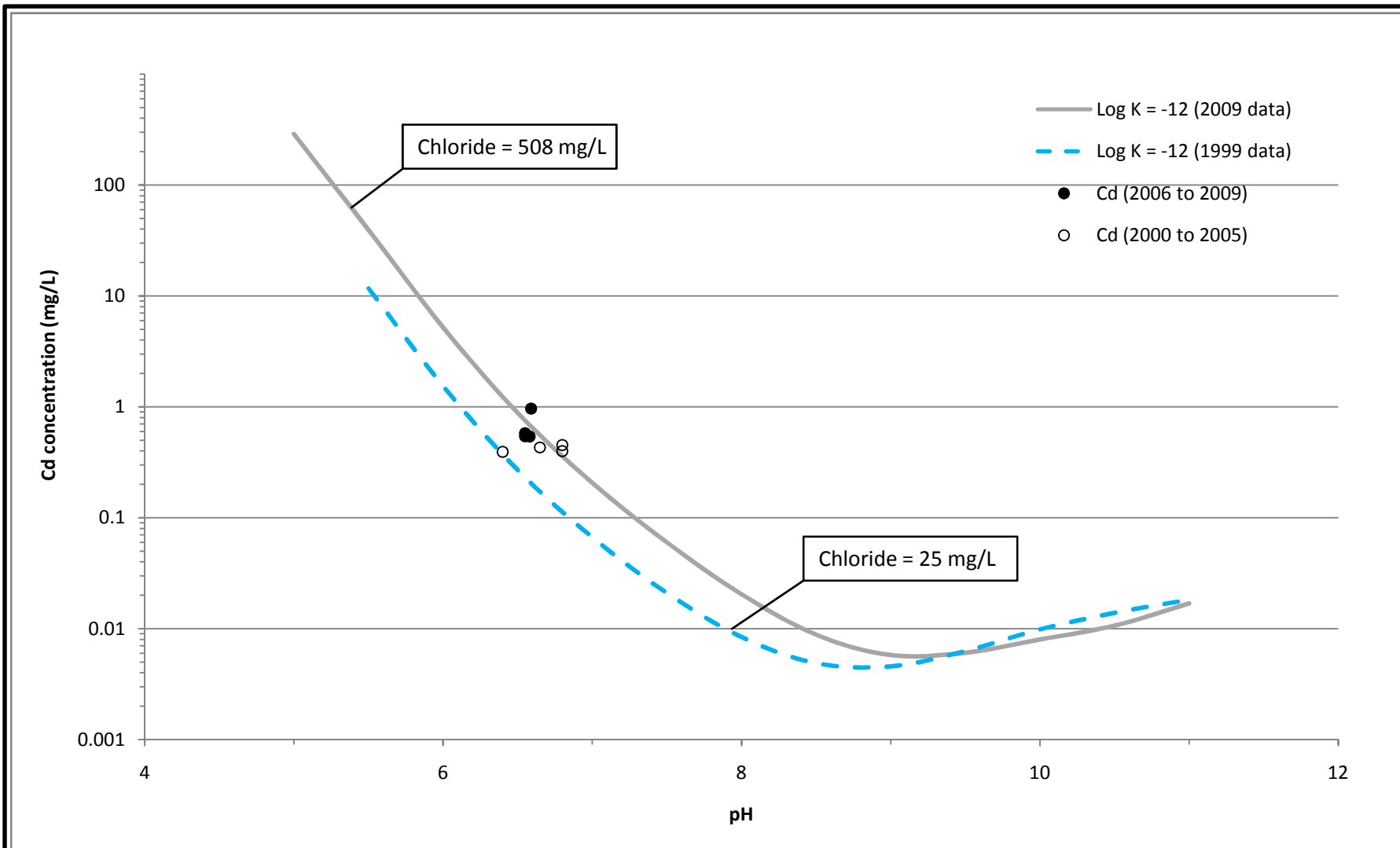
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Reviewed

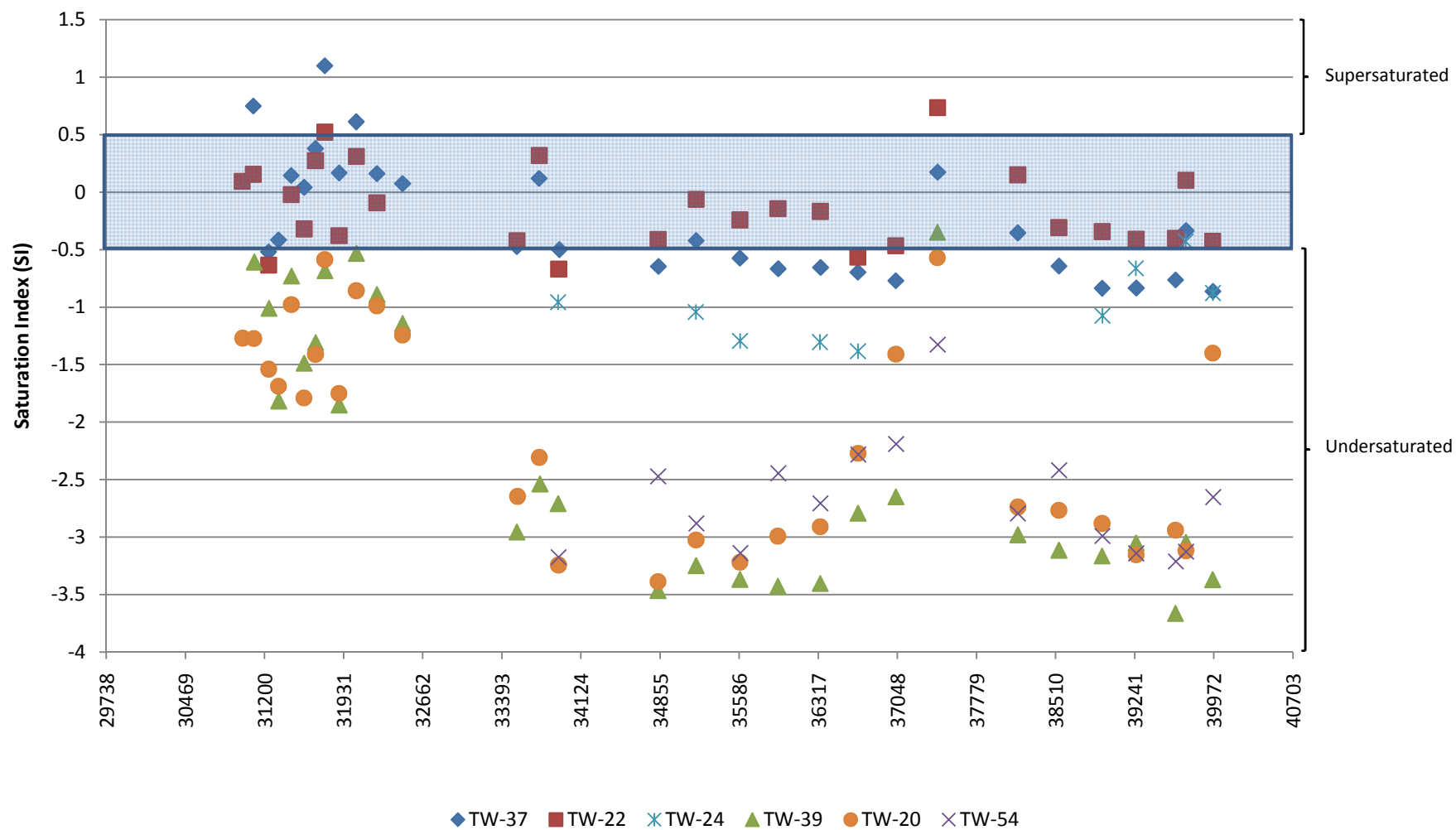
DB

FIGURE

12



Title		Otavite (CdCO ₃) solubility curve		Drawn	FV
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	CR
Client Name		Monsanto		Reviewed	DB
		Project No.	913-1101.605	FIGURE 13	
		Date	November 2009		



Title

UBZ-2 Rhodocrosite (MnCO_3) SI vs time

Project Name

Monsanto Soda Springs - Natural Attenuation

Project No.

913-1101.605

Client Name

Monsanto

Date

November 2009

Drawn

FV

Checked

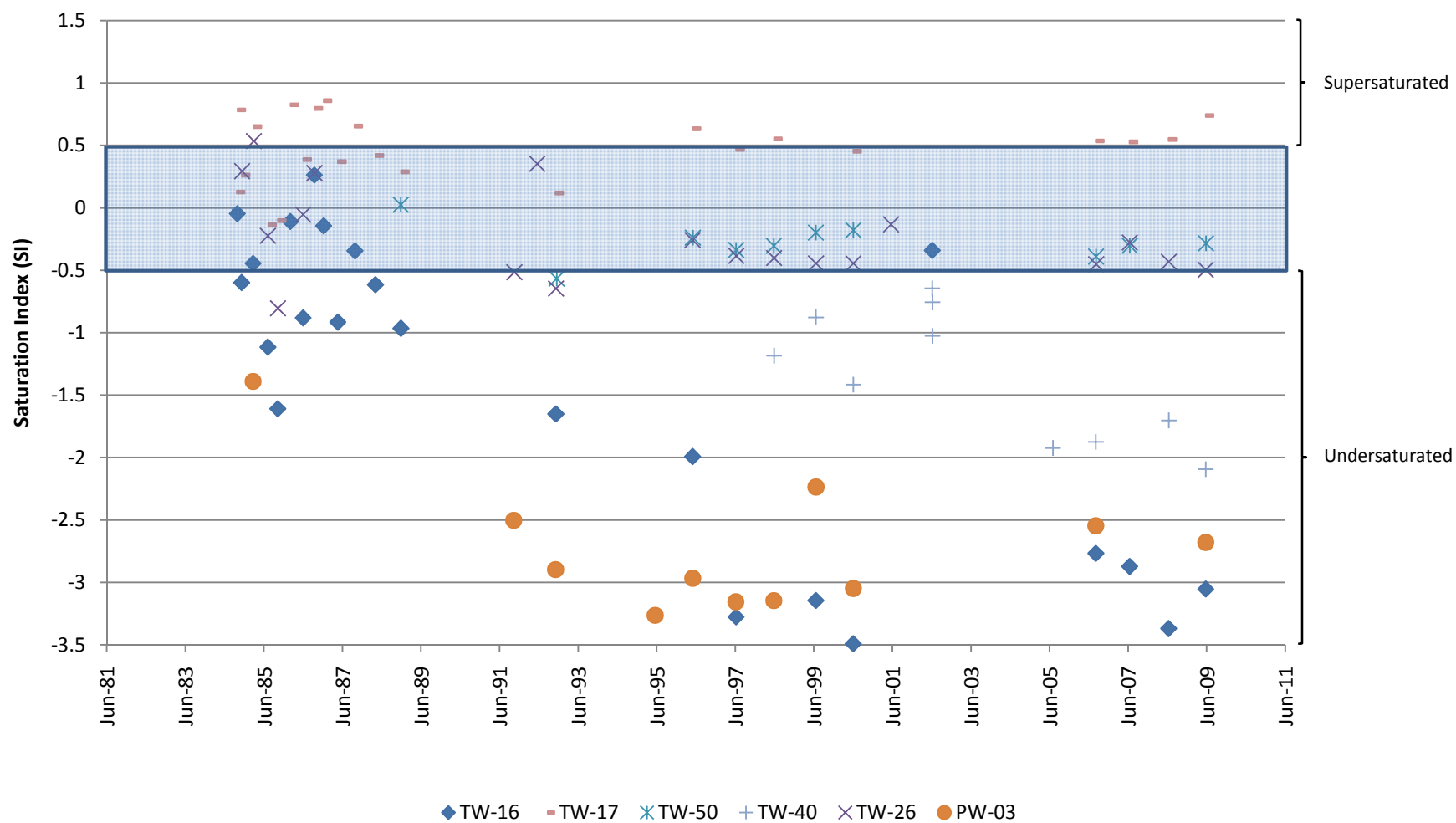
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Reviewed

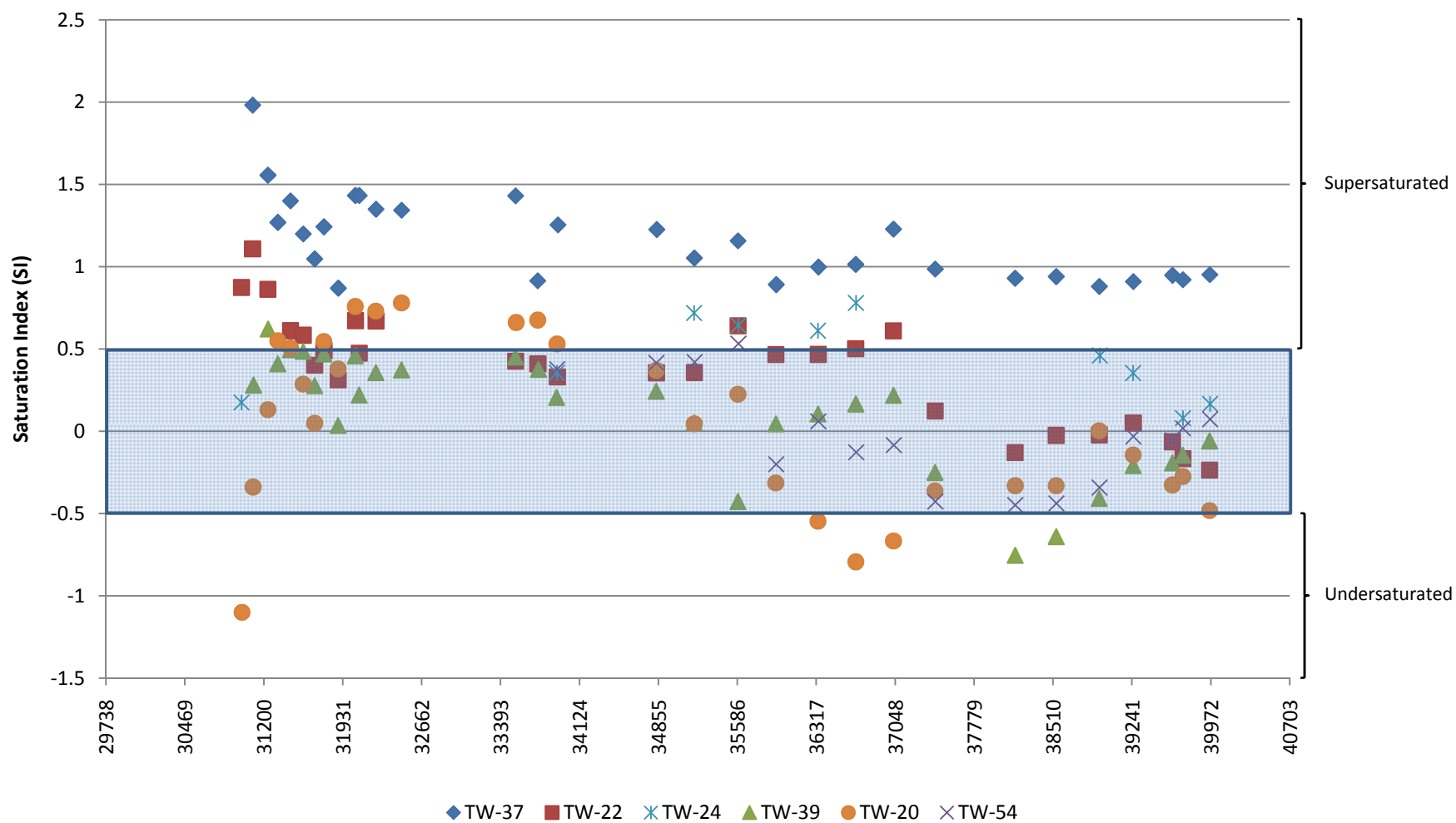
DB

FIGURE

14



Title		UBZ-4 Rhodocrosite (MnCO ₃) SI vs time		Drawn	FV
Project Name		Monsanto Soda Springs - Natural Attenuation		Checked	CR
Client Name		Monsanto		Reviewed	DB
		Project No.	913-1101.605	FIGURE 15	
		Date	November 2009		



Title

UBZ-2 Fluorite (CaF₂) SI vs time

Project Name

Monsanto Soda Springs - Natural Attenuation

Project No.

913-1101.605

Client Name

Monsanto

Date

November 2009

Drawn

FV

Checked

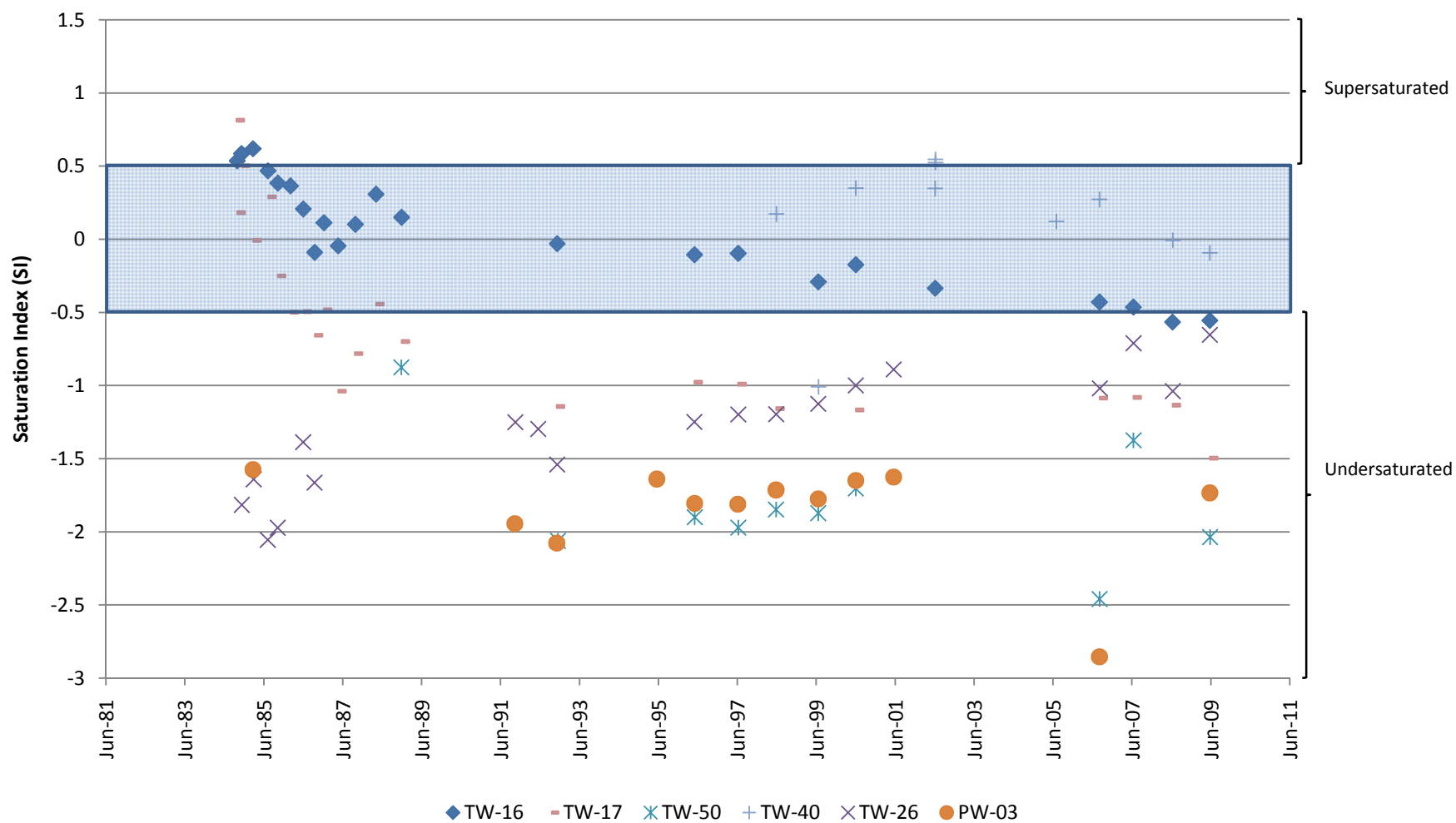
CR

Reviewed

DB

FIGURE

16



Title

UBZ-4 Fluorite (CaF₂) SI vs time

Project Name

Monsanto Soda Springs - Natural Attenuation

Project No.

913-1101.605

Client Name

Monsanto

Date

November 2009

Drawn

FV

Checked

CR

Reviewed

DB

FIGURE

17